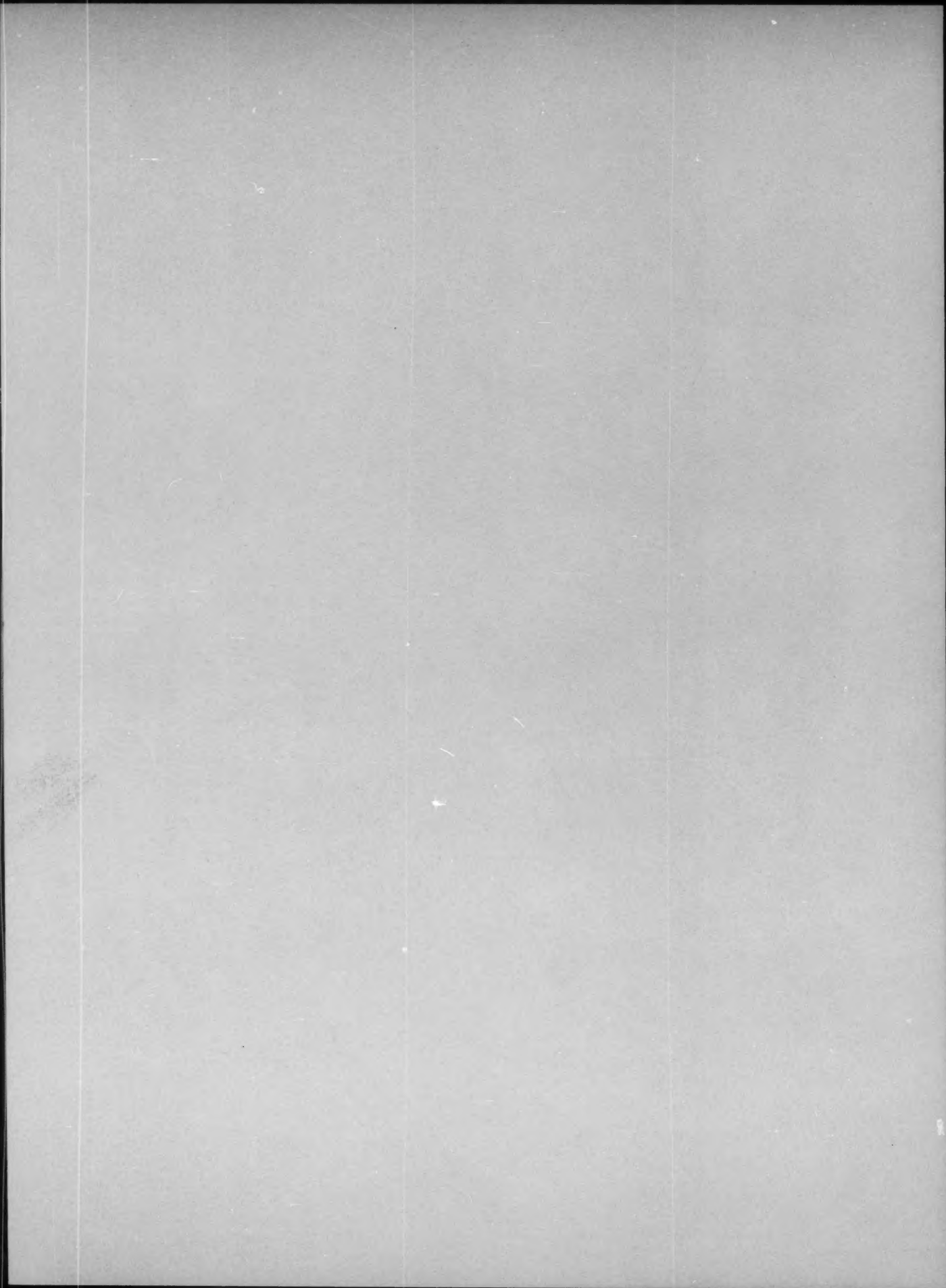


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Centenary of his birth

Yu. S. Musabekov

The life of the noted Russian chemist Mikhail Grigorevich Kucherov was not rich in external events, but on the other hand it was full of internal content and may be described as a solid achievement, adding still another illustrious page to the annals of natural science.

M. G. Kucherov, a native of Poltava province, spent all his conscious life in St. Petersburg. As a chemist he developed under the beneficial influence of the eminent Russian scientists M. N. Sokolov, A. N. Engelhardt, and P. A. Lachinov, whose closest associate he was and whom he succeeded in the Chair of the department. The early display of talent made it possible for Mikhail Grigorevich to become, at the age of 22, an assistant of Prof. Lachinov at the Forestry and Agriculture Institute. After the death of Lachinov, (1891) Kucherov was promoted to be docent and very quickly professor of the same Institute, in the laboratory of which all his brilliant experimental investigations were carried out.

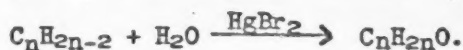
As early as 1873 the first paper by M. G. Kucherov appeared, dealing with the nitrile derivatives of diphenyl and the corresponding acids [1]. Two years afterwards P. A. Lachinov coupled the name of Kucherov, at a session of the Russian Chemical Society with the interesting phenomenon of the formation of ethyl acetate and acetylene by the action of alcoholic solutions of potassium acetate on vinyl bromide (at 160-170° [2]). Acetylene was formed by the action of dry silver nitrate on vinyl bromide at 150°. Subsequent papers by Kucherov [3] dealt, among other things with Lachinov's themes and were devoted to the substance called cholic acid [4], which was of much interest to Lachinov (according to him, cholic acid has the formula $C_{25}H_{42}O_5$). This period in the work of M. G. Kucherov may be termed that of preparation for independent investigation. But even here one can find it is possible to discern in the young scientist a critical attitude towards the work of other authors recommended to his attention. For instance, in a paper on the oxidation of cholic acid, Kucherov [3] experimentally refuted the results of the foreign scientist Tanneiner. The observations on cholic acid were continued by Mikhail Grigorevich until 1881 [5]. This year (1881) may be considered as the year of crisis in Kucherov's own development. By studying vinyl bromide, he was able to make the first observation of hydration of acetylene, and to the end of his long life he never left this field of work.

The predecessors of Kucherov in the study of the catalytic hydration of acetylene hydrocarbons were Zeize, Glinsky, and Eltekov. In 1867 in the Kazan Laboratory of A. M. Butlerov, Zeize and Glinsky showed that vinyl bromide and mercury acetate give acetaldehyde, which immediately reacts with $HgBr_2$, forming a white precipitate. Ten years later the Kharkov chemist A. P. Eltekov, studying vinyl derivatives, arrived at his well known rule concerning the instability of enols: "Alcohols, in which the hydroxyl radical is attached to a carbon atom having a free valency

(assuming the hypothesis of double bonds) can exist neither at high nor at ordinary temperatures, but they are, under the conditions of their formation transformed into aldehydes and ketones isomeric with them, this depending on whether the hydroxyl radical is attached to a terminal carbon atom or not" [6].

In Kucherov's paper "Observations on vinyl bromide" [7] the basic part of the investigation was devoted to the properties of vinyl bromide. About them Kucherov says: 1) that the bromine in the vinyl radical is strongly bound, as a result of which the substance does not show the usual double exchange reactions (displacement) without extensive rearrangement of the molecule; 2) that under the influence of alkalis, alcoholates and salts the substance decomposes either by the equation $C_2H_3Br \rightarrow C_2H_2 + HBr$ or else condenses. The latter remark of Kucherov's was the first statement of the ability of halogen vinyl derivatives to polymerize, a fact which has only acquired industrial importance recently - the production of polyvinyl chloride now runs into tens of thousands of tons per annum. But Kucherov makes, in the same paper, the observation which was important for the further development of his own work, that "by shaking acetylene with water and mercuric bromide, an aldehyde is produced even at ordinary temperatures. This reaction, which appears to be a general one for all the hydrocarbons of the acetylene series, will be described in detail in another communication" [7]. At the end of the paper the exact date of writing and the place where the work was done is appended: 26 March 1881, Chemical laboratory of the Forestry Institute.

Following this paper, in the same volume, is a preliminary communication about an extensive piece of work "New method of hydrating acetylene" [8]. Here the experimental detail is reported. The experiments on hydration Kucherov carried out in a flask with a long neck, capacity about a liter, into which was introduced water, mercuric bromide, and acetylene. After sealing off the neck of the flask it was heated on a water bath. The hydration reaction, general for all acetylenic hydrocarbons, proceeds according to the equation:



In this paper Kucherov stated that the reaction with allylene is quantitative and is smoother than with acetylene.

When the catalytic action of mercuric bromide on the hydration of acetylenic hydrocarbons was definitely established, Kucherov decided to extend the investigation to other salts of divalent mercury. In the record of the session of the Russian Chemical Society for 7 October 1882 [9] there is a report in which M. G. communicated the details of the catalytic hydration of allylene. According to his observations, the reactions proceed in two stages. In the first, molecular compounds of mercuric oxide with the hydrocarbon are formed, and, later there is a hydrolysis of this intermediate compound with the production of a ketone.

M. G. Kucherov's investigations on the hydration of unsaturated hydrocarbons were described by him more extensively in a long paper in 1883 [10]. In this work are described the details of experiments on the hydration of different hydrocarbons (acetylene, allylene, ethyl acetylene) in the presence of mercury derivatives (chloride, bromide, and iodide, the complex of the latter with KI, mercuric acetate), the detailed examination of the intermediate mercury organic compounds, their composition and structure. Considerable attention is given to the mechanism of the "Kucherov reaction", rules about the formation of aldehydes and ketones from acetylenic hydrocarbons are deduced, and so on.

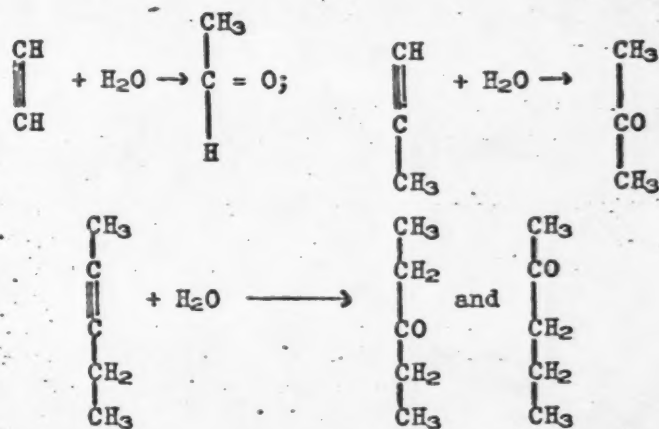
Among the important conclusions of this work was the fact that all divalent mercury compounds exert a catalytic action on this hydration to a greater or

lesser degree. The intermediate molecular mercury organic compound differs in composition from case to case very considerably, depending on the nature of the catalyst, and also on the acidity or alkalinity of the solution. Particularly complicated substances are formed in acid solution. Here molecular compounds were obtained which Kucherov considered as derivatives of the basic salt $C_3H_4 \cdot HgO$ (in the case of allylene) from which mercury is lost and ketones are formed when the environment is acid. In alkaline solution mercury atoms replace two atoms of hydrogen in two molecules of the hydrocarbon (thus, in the case of allylene forming the compound $(C_3H_3)_2Hg$) which is sufficiently simple in structure that acids can regenerate the original hydrocarbon (here allylene) from it. This mercury organic compound Kucherov compared with corresponding organic derivatives of acetylene with silver and copper. Consequently, if it is desired to hydrate acetylenes and obtain as a result aldehydes or ketones, it is necessary to carry out the reaction in alkaline solution.

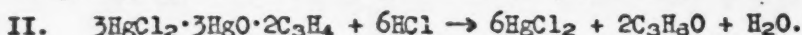
The hydration of acetylenes in acid solution proceeds smoothly in the presence of $HgCl_2$, $HgBr_2$, $HgSO_4$ and $(CH_3-COO)_2Hg$; HgI_2 however has hardly any catalytic action.

Kucherov considered that the process of catalytic hydration of acetylenes in acids may be made continuous, one and the same quantity of mercury salt serving for the hydration of an unlimited amount of hydrocarbon. In this way the reaction which he had studied resembles fermentation reactions (yeasts, etc.) in living organisms.

Kucherov formulated an extremely important rule for his experiments, which makes it possible to predict in advance the structure of the ketone to be expected from the hydration of the homologs of acetylene: "... in unsymmetrical hydrocarbons the hydrogen goes on to one of the triple bonded carbon atoms, and the oxygen goes on to the other triple bonded carbon atom which is not hydrogenated: in symmetrical hydrocarbons, the elements of water are distributed on each side of the triple bond, in all probability without any differentiation between the carbon atoms, and so, in the case of incompletely symmetrical hydrocarbons, two ketones may be expected ..." [10]. In accordance with his rule, Kucherov deduced the following representation for the catalytic hydration of acetylenes, which he had discovered:



Aldehyde is formed only from acetylene: all its homologs give ketones. By the detailed study of the composition of the intermediate molecular mercury compound Kucherov in the same work deduced equations representing both phases of the reaction. For instance allylene and mercuric chloride:



Both phases may be accomplished separately or simultaneously. In the latter case the first part of the process remains undiscoverable, and what is observed is simply the hydration.

M. G. Kucherov in this fundamental work in 1883 established the details and the structure of the complicated intermediate mercury complex. Scientists consider them as derivatives of a basic mercury salt with a cyclic structure, formed in accordance with the predictions of D. I. Mendeleev in his "New Chemistry". Kucherov considered this easy formation of molecular compounds of acetylenes with mercury salts which have a tendency to become converted to basic derivatives (chloride, sulfate, acetate) to be strong proof for the utility of his rule.

The work of Kucherov with mercury organic compounds was prolonged. In the proceedings of the session of the Chemical Society on December 5th, 1885, there is attached a report of Kucherov's on the preparation of metal carbonate and metal ammine compounds [12]. Six years later Kucherov reported to the Russian chemists about the action of mercury salt on diallyl and hydrocarbons and alcohols of the ethylenic series [13]. Thus, in the life of Mikhail Grigorevich Kucherov, Russian chemistry possesses one of its most devoted pioneers in the field of the investigation of metal organic compounds - a field in which, thanks to the work of A. N. Nesmeyanov, K. A. Kocheshkov and others, the Soviet Union is far in advance on the whole front.

To the study of the catalytic hydration of different organic compounds using mercury and other salts (silver, lead, potassium) Kucherov devoted nearly three decades. In the experimental work of Kucherov, his accurate methods for the quantitative determination of fusel oil in alcohols (1895) stands out with particular distinction. Kucherov's method consists in the extraction of the fusel oil with amyl alcohol in the presence of a saturated solution of sodium chloride and subsequent measurement of the oily layer in a graduated tube. The author proposed two variants: 1) a laboratory method with an accuracy of 0.017% and 2) a simplified one for plant practice with an accuracy of 0.1%.

The papers and communications of M. G. Kucherov are characterized by a meticulous description of all details, by the easy reproducibility of the experiment and the persuasiveness of the conclusions. It is evident that in this the beneficial influence of N. N. Sokolov appeared. Sokolov sharply criticized some French chemists for their writings, which did not make it possible to repeat and check their experiments. The exclusive talent of Kucherov was characterized thus in the most positive manner.

The long paper by Kucherov, devoted to the memory of P. A. Lachinov deserves special study [14]. In it M. G. shows himself to have had a good knowledge of this history of science, to be a critic, a master of original artistic description, a psychologist and even in certain cases not a bad expositor of the phenomena of scientific life against the general social economic background of the country. The remarkable sixty years, he characterized for example in the following words: "It is well known to all that in this epoch, short but full of incidents, everything was seized with an impulse for the renewal of old forms of existence. Even the schools, particularly the professional ones, did not escape this. The abolition of serfdom, regenerating the whole economic order, forced us to think of new bases and methods of production in industry. To be ignorant of science became impossible". In this outline Kucherov gave the best characterization of all of N. N. Sokolov, P. A. Lachinov and the workers in the chemical laboratory of the Forestry Institute.

The description reflects the state of mind of Kucherov so clearly that we reproduce here the whole section from his paper:

"Only after a year did the laboratory awake from its torpor. N. N. Sokolov appeared. Shortly after him, in the same year, P. A. returned also.

The name of Sokolov was well known to all of us. Not without some sinking of our hearts did we look forward to seeing in person the man, who had been mentioned so often and so honorably by P. A., whose distinguished papers in the Chemical Journal we had read with such pleasure, whom rumour recommended as a remarkable example of a human being The man we saw completely corresponded with the stately form created in our imagination. The energy of his spirit to a great extent overcame his physical ill-health and his cheerful presence inspired all of us, his closest associate and students, to make wide use of the influence of his unusual teaching abilities, of his untiring readiness to instruct and of the fascination of his fair and noble countenance. We cannot forget with what sincerity and goodwill, and how completely naturally, he became one of us all; with what joy and wealth of explanation, not sparing his weak eyesight nor his weak chest he would most painstakingly sometimes continue in one or another operation, which was not without its hazards, if he found in it the slightest degree of interest. We shall never forget those happy hours, when over a drink, he started to chat. P. A. nearly always participated in these conversations as well These chats, thanks fortunately to the complicated external conditions, were for us and for P. A. as well more than simple pleasures, more even than enjoyment. We all lived under one roof. The laboratory was open at every hour of the day and night. N. N. Sokolov's flat was near the laboratory; we often stayed up far past midnight: N. N. did the same. Consequently not only at every hour of the day but also it can be said at every hour of the night these conversations might proceed. Such a state of affairs lasted six whole years. We did not talk about incidental points of interest, but of a complete system of instruction. The whole man participated with all the treasures of his powerful mind and rich experience; of his deeply critical intellect an intellect amazingly clear, accurate, fertile and quick. His education was splendid and so versatile that hardly any intellectual or moral interest escaped him; his kind of knowledge was so inexhaustible and fundamental that it could only have been obtained at first hand, and was so well preserved that it was not clear how it could have resisted the all-destroying hand of time. He drew on his immeasurable store of many-sided reminiscences and observations, drawn from many countries of Europe and many parts of Russia, which provided him with an inexhaustible source of material for illustrating or supporting any question that might crop up at any moment. Finally, his amazing expertness in work also was demonstrated on these occasions, and no less clearly in evidence was his majestic countenance - a spirit towering high above the commonplace of everyday existence, devoted to the search for truth without the slightest suspicion of mercenary motive, a spirit proud, independent, and so self-sufficient that his equanimity was maintained under the strongest of all human temptations - the temptation of fame.

The respect of P. A. for Sokolov went as far as reverence. In his turn Sokolov loved P. A. sincerely.... " (575-576).

The works of Kucherov exerted a powerful effect on the development of chemical science and industry, both in Russia and in the rest of the world. In the history of science not a few examples are met with of interesting scientific discoveries made in the laboratory, not finding use in industry for a decade or more; and it was particularly harmful that due to the social and economic backwardness of the country and the musty atmosphere of servility to everything foreign, many Russian chemical discoveries found their initial industrial appli-

cation abroad. Foreign lovers of profit-at-another's-expense utilized Kucherov's reaction. The "incubation period" [15] for Kucherov's reactions was, for example, a third of a century; the manufacture of acetaldehyde from acetylene by hydration in the presence of mercuric sulfate in chemical plants did not get going until thirty three years after Kucherov's discovery. The enormous scale on which his synthesis is used has been achieved only in our own times. Nowadays, acetaldehyde is obtained from acetylene at the rate of more than three hundred thousand tons per year.

M. G. Kucherov, extending the best tradition of his predecessors, labored hard and most fruitfully for the greatest advancement of Russian chemistry. Nearly all his works were published in the "Journal of the Russian Chemical Society", of which he was an active member for many years. In 1885 the Chemical Society presented him with the "N. N. Sokolov Award",¹ for his contribution to science - the discovery and study of the reactions of acetylenic hydrocarbons with compounds of mercury [19].

M. G. Kucherov was in all things worthy of the continued thanks of his students. The intercourse of M. G. with the youth of those times whose disposition was revolutionary (the Kravchinsky brothers, and others) converted Kucherov to a progressive worker in the high school.

It is regrettable that as yet no creative biography of M. G. Kucherov has placed on record his influence on the history of science. The few lines about him in the works of P. I. Walden [20], M. A. Bloch [21] and the "Great Soviet Encyclopedia" [22] are quite inadequate. This review does not pretend to be complete. Our native chemical science is truly honored by the works of Mikhail Grigorevich Kucherov; his life and activity await their biographer.

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¹) This prize was established with a gift by the famous thermochemist and revolutionary V.F. Luginin in 1880 [16] and was awarded in 1888 as well to M.G. Kucherov, N.A. Menshutkin [17], G.G. Gustavson, and A.E. Favorsky. The Commission of the Chemical Society has awarded the P.A. Sokolov prize to A.M. Butlerov, D.I. Mendeleev, N.A. Menshutkin, P.A. Lachinova, and K.I. Lysenko, [18].

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PREPARATION OF POTASSIUM PERMANGANATE AND MANGANATE BY

ANODIC SOLUTION OF METALLIC MANGANESE

R. I. Agladze and G. M. Domanskaya

It is interesting that after Shall, Beketov worked on the structure of manganates as long ago as the fifties of the last century [1]. Manganates are only stable in alkaline solution. The original method for the manufacture of permanganate made use of this fact, and manganates were dissolved in water. This causes the manganate to decompose with the formation of permanganate: $3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$. This reaction can easily be carried to completion if the alkali formed is neutralized. This may be achieved by saturating the solution with carbon dioxide. Experiments on the preparation of permanganates by anodic solution of manganiferous alloys in solutions of caustic alkalies or carbonates have been carried out by a series of investigators [2]. Patents have even been taken out abroad on this method of producing permanganates, but, as far as we know, no experiments on the industrial utilization of ferromanganese and silicomanganese have given positive results, since after a short period of working, the anodes become passivated and the voltage across the terminals increases. Grube and Metzger [4], and also Lubyantsev and Bakhchisaraitsyants in their extensive investigation [5] aimed at removing the passivation of the anodes, imposed considerable changes of current upon the electrodes, without attaining the desired results.

One of the authors of the present paper has published the results of work on the preparation of metallic manganese by electrolysis [3]. The possession of electrolytic manganese made it possible to carry out experiments on the anodic solution of pure manganese in alkalies. As our experiments showed, when electrolytic manganese was used, passivation of the anodes, which had made it impossible to use manganese alloys for the production of permanganates, did not occur. The preliminary report on our experiments on the anodic solution of manganese was made by us as early as 1947.

EXPERIMENTAL

Description of the apparatus. Manganese is very hard and brittle, so that it is difficult to work, and therefore rectangular electrodes were cut out with a diamond from the electrolytic plates obtained. Where necessary, the exterior dendritic surface of the electrode was worked off on a grinding bench with a corundum wheel. The smooth surface of the plate was rubbed down with fine emery cloth. After each experiment the plates were washed with dilute nitric acid, followed by distilled water.

To convey current to the plates the wire was fixed to them either with brass terminals, or simply soldered on with tin. It should be mentioned that soldering to manganese with tin is difficult and that the bonds made in this fashion frequently parted. Nickel plates were used. A beaker was used as a cell, its capacity being about 150 ml. The cathode and anode were mounted in

an ebonite plate, which was laid across the top of the beaker. The cell was immersed in a thermostat. A selenium rectifier was used as a source of current, and in some cases a battery of accumulators. The electrolytic manganese used for the anode contained 99.9% Mn.

The method of analysis of the products of electrolysis. After carrying out an experiment the electrolyte was usually a mixture of potassium permanganate and manganate, with a certain quantity of slime, consisting of manganese oxides and hydroxides. The solution was filtered in order to separate it from the slime. To determine the quantity of manganese in the slime, the precipitate on the filter was dissolved in concentrated hydrochloric acid and the manganese in the solution was determined by Volhard's method. The filtrate, according to the conditions of the experiment, contained either manganate or permanganate. In cases where permanganate was to be obtained, sulfuric acid was added to the solution in quantity sufficient not only to neutralize the alkali, but also to leave the solution strongly acid. This acidity was necessary to reduce the seven-valent manganese to the divalent condition with sodium oxalate. After diluting the solution with hot water, we added an excess of sodium oxalate to it. Later this excess was back titrated with potassium permanganate. The amount of permanganate could then be calculated from the amount of the reducing agent which had been consumed. In the second case, that is when the solution was alkaline and manganate was obtained, the solution was also acidified at the beginning as before. However, while the acidity of the solution facilitated the stabilization of permanganate, the manganate was decomposed with formation of permanganate and manganese dioxide. In the presence of an excess of sulfuric acid, oxalic acid reduced the permanganate as well to manganese dioxide.

Effect of concentration of the electrolyte. For the study of the effect of variations of concentration of alkali, the temperature of the electrolyte, and the anode current density, in the electrolytic solution of manganese or its alloys in alkalies, solutions were prepared containing manganese in different states of oxidation. In strongly alkaline solution and at high temperatures the permanganate is reduced to manganate with liberation of oxygen according to the reaction:



To determine the effect of the concentration of caustic alkali on the process of the anodic solution of manganese, a series of preliminary experiments were carried out. In the course of these we observed in weak alkaline solution (6-8%) a crimson coloration characteristic of permanganate around the anode during electrolysis. This coloration of the electrolyte remained unchanged in experiments which lasted more than one hour. An altogether different picture was observed in the electrolysis of solutions of moderate alkali concentration. After switching on the current, streams of crimson electrolyte could be seen leaving the manganese anode, rapidly changing to green: when the experiment was prolonged the solution became dark blue in color, which appeared to be a result of the mixture of the dark crimson color of a saturated solution of the permanganate and the dark green of the manganate.

In concentrated (30% and higher) alkali solutions, the space around the anode and afterwards the whole of the electrolyte took on the green color of manganate from the very start of the experiment. Manganate-permanganate mixtures differ considerably in stability, and their relative concentrations depend upon the alkalinity of the bath, the temperature and other factors.

In Table 1 are set out the results of experiments which we carried out in order to elucidate the effect of the concentration of KOH on the process of anodic solution of manganese. When dissolving manganese in solutions of alkali carbonates under different conditions, we obtained potassium permanganate alone in all experiments. The non-formation of manganate in alkali carbonate solutions may be attributed first to the fact that the alkalinity of these solutions is lower and second to the fact that in the presence of carbonate, manganate, even if it formed, slowly reverts to permanganate with simultaneous formation of the dioxide according to the scheme:



From the data set out in Table 2 it is evident that in electrolytes consisting of aqueous solutions of potassium carbonate, the current yield depends to only a small extent on the concentration of the electrolyte, and only when the concentration of the solution falls below 50 g/liter does the current yield fall off to any marked extent. The yield of product (ratio of the quantity of manganese, going into solution in the form of permanganate to the total quantity of manganese found in the slime and in the solution) depends to only a small extent on the concentration of the electrolyte. The voltage on the bath, as a result of changes in the electrical resistance between the electrodes, increases both when the electrolyte is diluted (and in amount proportional to this dilution) and also when the electrolyte becomes supersaturated with salts, and crystals are deposited on the electrodes. As a result of the increased voltage the consumption of electrical energy per g of permanganate increases. We observed a specific consumption of electrical energy of about 16 kw/kg when using solutions containing from 300-500 g/liter K_2CO_3 . With this solution the current yield was about 20%.

Effect of temperature. The results of three series of experiments carried on for different periods of time with 37% KOH are set forth in Table 3. At this concentration of alkali the solution only contained manganate. The current yield of manganate increases as the temperature increases. At the same time, as a result of the increase of the electrical conductivity of the electrolyte and a fall in the c.d. across the bath, the consumption of electrical energy decreased; however in all cases the yield of product decreased. Particularly large amounts of dioxide were formed at temperatures above 60°.

From the data of experiments of the third series it is evident that taking all factors into consideration (current yield, energy and product yield) the optimum temperature should be taken as around 20° at which, with an energy consumption of 20 kw/kg, the yield of product in the form of manganate was 70%. The expression 'product yield' here implies the result of multiplying by 100 the ratio of the quantity of manganese contained in the manganate to the general quantity of anodically dissolved manganese, which went not only into solution as manganate, but was also precipitated in the slime, where it was present mainly in the form of hydrated manganese dioxide.

The results of experiments show (Table 4) that the best results with a carbonate electrolyte are obtained in the temperature range of 15-35°.

Effect of anodic current density | Experiments with electrolytes containing caustic potash were carried out in two series. Table 5 contains the results of experiments carried out with 37% KOH at an anode c.d. of 2-28 A/dm². The for-

TABLE 1

Effect of concentration of the electrolyte on the process of anodic solution of electrolytic manganese in KOH¹⁾

Concentration of KOH (in %)	Current density of the anode (in A/dm ²)	Oxidizing power of the electrolyte (in ml of 0.1 N Na ₂ C ₂ O ₄)
47	7.7	58.4
47	7.7	54.9
47	12.5	69.0
47	12.5	63.3
37	7.7	32.4
37	12.5	39.9
21	7.7	12.3
21	12.5	15.4
11	7.7	5.7
11	12.5	5.4

mation of the ions containing manganese in a higher state of oxidation, requires a definite potential across the electrolyte, so that when the potential was lower the formation of ions corresponding to a lower state of oxidation was observed - mainly with manganese having the oxidation number 6. It should be mentioned that the favorable zone of potential for the formation of ions in the higher state of oxidation changes as a function of the nature of the electrolyte and the temperature. During the experiment, carried out at an anode c.d. of 2 A/dm², only traces of manganate were detected in the electrolyte, in which the potential across the terminals, which initially was 2.2 V, had

risen by the end to 2.4 V. In this case there are formed in the solution ions containing manganese in a lower state of oxidation. The manganese hydroxide thus obtained deposits on the anode and causes the potential across the bath to increase. The traces of manganate observed in the case in point originate, in our opinion, from the further oxidation on the anode of hydrates of lower valent compounds of manganese. For manganate there was observed quite a considerable increase in current yield as the current density was increased; notwithstanding the increased p.d. the specific energy consumption decreases from 22 kw at 6.2 A/dm² to 16 kw at 21-28 A/dm². Since in the course of this series of experiments we did not secure the complete removal of all excess heat from the cell at large current densities, we started an additional series of experiments in which all measurements were made at constant temperature. This series of experiments (Table 6) was carried out with more concentrated KOH (47%). At a current density of 18 A/dm² a maximum current yield was observed which reached 22.6% at a product yield of 92%.

TABLE 2

Effect of concentration of electrolyte on the process of anodic solution of manganese in solutions of K₂CO₃

Duration of experiments 40 minutes. Temperatures 25-48°. Anodic current density 6 A/dm². 25 A/dm² on the cathode.

Concentration of the solution (g/l)	P.D.	Quantity of Mn leaving the anode (g)		Current yield for KMnO ₄ (%)	Product yield (%)	Consumption of energy (in kw/kg of KMnO ₄)
		Entering solution as KMnO ₄	Going into the slime			
820	4.9	0.0376	-	24.0	-	-
600	4.1	0.0379	0.0077	24.0	83	20
480	3.6	0.0410	-	26.3	-	16
360	3.7	0.0390	0.0070	25.0	85	-
240	3.9	0.0383	0.0080	24.6	83	19
120	4.5	0.0359	0.0080	23.0	82	23
60	5.6	0.0369	0.0030	23.0	82	28
36	7.8	0.0248	-	16.0	-	61

1) Duration of the experiments 20 minutes; current density at the anode 33 A/dm².

TABLE 3

Effect of electrolyte temperature on the process of anodic solution of manganese in a 37%-M solution of KOH

Duration of experiments of the first series 75 minutes, of the second and third series 60 minutes. Current density on the anode 8 A/dm², on the cathode 31 A/dm²

Test series	Temperature (in °)	P.D.	Quantity of Mn leaving the anode (g)		Current yield for K ₂ MnO ₄ (%)	Product yield (%)	Consumption of energy (in kw/kg of K ₂ MnO ₄)
			Entering solution as K ₂ MnO ₄	Going into the slime			
1	15	3.5	0.043	-	10.1	-	28.0
	17	3.5	0.048	0.017	10.3	73	25.7
	31	3.1	0.028	0.017	6.5	62	37.2
	41-42	3.0	0.036	0.024	8.5	56	29.0
	48	3.0	0.030	-	7.2	-	31.6
	60	2.8	0.031	-	7.3	-	-
	70	2.6	0.055	-	13.4	-	16.2
2	66-70	2.6	0.052	-	12.3	-	17.0
	15	3.7	0.044	-	13.0	-	23.0
	31-33	3.5	0.029	-	8.7	-	33.0
3	61-63	3.0	0.033	0.022	10.0	60	25.0
	17-18	3.4	0.058	0.023	12.9	71	21.5
	18	3.4	0.056	0.023	12.5	71	22.0
	33	3.1	0.038	0.023	8.6	62	29.4
	35-36	3.1	0.034	0.023	7.7	60	32.8
	60-63	2.9	0.035	0.022	7.8	62	22.2
	72-74	2.5	0.047	0.024	10.4	66	18.8
	94-96	2.7	0.087	0.071	19.3	57	11.4

TABLE 4

Effect of electrolyte temperature on the process of anodic solution of manganese in 23%-M solution of K₂CO₃

Duration of experiment 40 minutes. Anode current density 6 A/dm².

Cathode current density 27 A/dm²

Temperature (in °)	P.D.	Quantity of Mn leaving the anode (g)		Current yield for KMnO ₄ (%)	Product yield (%)	Consumption of energy (in kw/kg of KMnO ₄)
		Entering solution as KMnO ₄	Going into the slime			
3-7	4.2	0.014	-	9.3	-	34.0
15	4.1	0.037	0.004	23.7	90.4	20.0
17	4.1	0.037	0.004	23.5	90.4	20.0
30-32	3.6	0.038	0.005	21.7	88.0	19.3
45-48	3.2	0.029	0.010	18.8	76.0	20.0
56-57	3.1	0.023	0.010	15.0	69.0	24.3
70-72	2.8	0.018	0.012	11.5	60.0	27.0
92-94	2.9	0.018	0.018	10.4	50.0	32.0

TABLE 5

Effect of anode current density on the process of anodic solution of manganese in 37%-M solution of KOH

Duration of experiment 90 minutes

Voltage (V)	Temperature (°C)	Current density (A/dm ²)		K ₂ MnO ₄ obtained (g)	Current yield for K ₂ MnO ₄ (%)	Energy consumption (kw/kg K ₂ MnO ₄)
		On anode	On cathode			
2.2-2.4	15	2.0	5.3	-	-	-
2.6	16	4.0	15.6	0.091	9.84	21.4
2.9	16	6.2	23.1	0.163	11.80	22.2
3.2	17	8.3	31.2	0.260	14.00	18.4
3.3	17	10.0	38.7	0.328	14.80	18.1
3.5	20	13.3	50	0.500	17.00	16.8
3.8	21	16.6	62	0.628	18.50	16.9
4.0	19	21.0	75	0.894	20.00	16.0
4.4	25	24.0	87	1.175	22.60	15.7
4.6	26	28.0	94	1.925	23.30	16.0

TABLE 6

Effect of anode current density on the process of anodic solution of manganese in 47%-M solution of KOH

Duration of experiment 60 minutes. Temperature 25°.

Current density (A/dm ²)		Quantity of Mn leaving the anode (in g)		Current yield for K ₂ MnO ₄ in %	Product yield in %
On anode	On cathode	Entering solution as K ₂ MnO ₄	In slime		
14.3	45	0.092	0.009	20.6	91.0
18.0	57	0.124	0.011	22.6	92.0
21.4	68	0.145	0.011	21.6	93.0
23.5	80	0.168	0.017	20.7	90.6
28.6	91	0.163	0.013	18.3	92.7

TABLE 7

Influence of anode current density on the process of anodic solution of manganese in 29%-M solution of K₂CO₃

Duration of experiment 40 minutes. Temperature 14-15°.

Voltage (V)	Current Density (A/dm ²)		Quantity of Mn leaving the anode (in g)		Current yield for KMnO ₄ (%)	Product yield (%)	Energy expenditure (kw/kg KMnO ₄)
	On anode	On cathode	Entering solution as KMnO ₄	In slime			
2.8	2.4	6.3	0.006	-	15.0	-	21.0
2.6	3.7	9.1	0.016	0.0055	28.6	74	10.7
4.1	7.2	19.0	0.028	0.0043	24.5	88	19.9
4.4	10.6	28.0	0.048	0.0040	27.6	92	15.9
4.7	14.3	38.0	0.067	0.0049	28.9	93	19.1
5.2	17.9	47.0	0.082	0.0130	28.4	86	21.6

Table 7 gives figures showing the effect of current density on the process of formation of potassium permanganate. These experiments were carried out with 29% K_2CO_3 at an anode c.d. of 2.4-17.9 A/dm² at a temperature of 14-15°. At a lower current density (2.4 A/dm²) we observed, as with the KOH solutions, an increase in the voltage and a relatively small current yield towards the end of the experiment. The minimum energy consumption of 10.7 kv/kg of permanganate occurred at an anode c.d. of 3.7 A/dm². At this the current yield was 26.6%. With further increase in the c.d. the current yield, it is true, did not change sharply but on account of the increase in the p.d. the specific energy consumption increased.

Influence of anode c.d.: cathode c.d. ratio. Table 3 contains the results of a series of experiments with 29% K_2CO_3 carried out at different values of the ratio of anode to cathode c.d. In these experiments the anode c.d. was maintained at 14.7 A/dm², while the cathode c.d. was varied from 6.3 to 111 A/dm². Such a change in the c.d. ratio did not cause any considerable change in the current or product yields, but the specific energy consumption decreased with increase in the ratio, due to the lowering of the general p.d. across the bath.

Effect of inter-electrode distance. The effect of distance between the electrodes was studied only with 47% KOH (Table 9). The results set out in the table show that the current yield increases little with increase of inter-electrode distance. This is possibly connected with a decrease in the quantity of the higher valent manganese compound reduced on the cathode.

TABLE 8

Effect of ratio of anode to cathode c.d. on the process of anodic solution of manganese in 29%-M solution of K_2CO_3

Duration of experiment 40 minutes. Anode c.d. 14.7 A/dm².
Temperature 16°.

Anode cathode c.d. ratio	Voltage (v)	Cathode c.d. (A/dm ²)	Quantity of Mn leaving the anode (g)		Current yield for KMnO ₄ (%)	Product yield (%)	Energy consumption (kv/kg KMnO ₄)
			Entering solution as KMnO ₄	In slime			
0.18	5.3	111	0.058	0.009	30.0	87	21.0
0.26	4.9	55	0.058	0.008	30.0	88	19.0
0.29	4.8	50	0.056	-	27.8	-	19.0
0.70	4.4	21	0.056	0.006	29.2	90	18.0
1.10	4.2	13	0.055	0.007	28.6	88	17.4
1.47	3.9	10	0.053	0.006	27.0	88	16.8
2.30	4.0	6.3	0.058	-	30.0	-	15.6

Effect of stirring electrolyte and rotating anode. In the anodic solution of manganese it would be expected that the concentration of alkali which combines with the manganese would decrease during the experiment in the layer near the anode. Hence, there might be expected some beneficial effect of stirring the electrolyte and rotating the anode. In Table 10 are set forth the results of experiments made both with stirred and unstirred electrolyte, and also with a rotating anode. The increase in consumption of energy when the anode was rotated is due to an increase in the potential across the bath due to the special contacts which were used to feed current to the rotating anode. The results we obtained in experiments by using 47% KOH as electrolyte showed a certain improvement in the process when stirring was employed. While in the absence of stirring

TABLE 9

Effect of distance between electrodes on the process of anodic solution of manganese in 47% M solution of KOH

Duration of experiment 19 minutes. Temperature 18-20°.

Distance between electrodes (cm)	Voltage (v)	C.D. (A/dm ²)		Quantity of Mn leaving the anode (g)		Current yield for K ₂ MnO ₄ (%)	Product yield (%)	Energy consumption (kw/kg K ₂ MnO ₄)
		On anode	On cathode	Entering solution as K ₂ MnO ₄	In slime			
4.2	4.0	9.6	62.5	0.0827	0.0087	24.4	90	13.3
3.2	3.8	9.6	62.5	0.0783	0.0084	23.1	91	13.3
2.2	3.6	9.6	62.5	0.0811	0.0085	23.9	91	12.3
1.5	3.6	9.6	62.5	0.0760	0.012	22.4	86	13.0
4.5	4.2	7.9	26.6	0.1030	0.009	25.3	92	13.4
3.5	3.5	7.9	26.6	0.1010	0.010	24.8	91	11.5
2.5	3.5	7.9	26.6	0.0980	-	24.1	-	11.4
1.5	3.4	7.9	26.6	0.0980	0.009	24.1	92	11.4
0.8	3.3	7.9	26.6	0.0990	0.010	24.3	91	11.1

TABLE 10

Effect of mixing electrolyte and rotating electrode on the process of anodic solution of manganese in 47% M solution of KOH

Duration of experiment 40 minutes. Anode c.d. 6.6 A/dm². Temperature 18°.

Voltage (v)	Cathode c.d. (A/dm ²)	Quantity of Mn leaving the anode (g)		Current yield of K ₂ MnO ₄ (%)	Product yield (%)	Energy consumption (kw/kg K ₂ MnO ₄)	Remarks
		Entering solution as K ₂ MnO ₄	In slime				
3.8	32	0.078	0.013	18.6	85.6	15.9	Electrolyte not stirred.
3.8	32	0.081	0.013	19.9	86.0	15.5	Electrolyte stirred at 120 rpm.
3.8	32	0.085	0.012	21.0	88.0	14.4	Electrolyte stirred at 250 rpm.
4.6	28	0.095	0.009	23.8	91.0	16.0	Anode rotated.

the current yield was 18.6%, when the electrolyte was stirred it reached 23.8%, and at the same time there was some improvement in the product yield (85.6-91%).

Effect of duration of experiment. We have already noted that the anodic solution of manganese alloy always ran into the difficulty of the formation of a passive film on the anode. This film, varying in chemical and mechanical strength, raised the voltage on the bath to values of the order of 100 V and the formation of this film caused the process of electrolysis to cease completely.

In experiments we carried out with anodes of electrolytic manganese and with various electrolytes, no such film was formed, the process of electrolysis did not cease, and the potential on the bath did not change its value even during ex-

periments of long duration. However, when using electrolytes which contained neither manganate nor permanganate, or an anode with a freshly rubbed down surface, the current yield was always somewhat better than in prolonged experiments, where the surface of the electrode became dark due to the formation on it of a thin layer of oxides. It was observed that when using carbonates in the electrolyte the anode had a cinnamon shade, and when using caustic alkali a black shade, characteristic of manganese dioxide. We carried out prolonged experiments on the anodic solution of manganese with 46% KOH. 25.8 Ah. were passed through the solution in the course of 46 hours. The p.d. was 3.0-3.2 V. The change in potential is shown by the following figures:

Duration in hours	0	2	4	12	24	36	43
Voltage	3.0	3.0	3.1	3.1	3.1	3.2	3.2

The submerged part of the anode at the beginning of the experiment was 7 cm², but by the end of the experiment so much of the anode had dissolved that this surface had diminished to 4 cm². At the end of the experiment the c.d. therefore had increased. The increase of potential on the bath was conditioned by this increase in c.d. and also by the fact that the anode was covered by crystals of potassium permanganate. Crystals of permanganate also were observed on the floor of the cell; the solution contained potassium manganate. The presence of crystals of permanganate in the alkaline solution may be explained by the fact that at the end of electrolysis in this particular case the c.d. was higher, which facilitated the oxidation of part of the manganate to permanganate. Near the anode, where a certain acidification of the solution occurred, part of the manganate oxidized to permanganate, and since the solubility of permanganate in strong alkali is very small it crystallized and deposited on the anode. Some of these crystals fell off and accumulated on the floor of the cell. The current yield of potassium manganate was 27.7%. The permanganate crystals were dissolved and their quantity determined; the result indicated a current yield for permanganate of 8.8%. The total product yield was 81%. The results of two additional experiments are set forth in Table 11.

TABLE 11

Results of experiments of anodic solution of manganese in 46%-M solution of KOH. Duration of experiment 43 hours. Temperature of experiment 28°. Electrolyte volume 70 ml, volume of electrolyte participating in the experiment 350 ml.

Voltage (v)	C.D. (A/dm ²)		Current yield for K ₂ MnO ₄ (%)	Current yield for KMnO ₄ (%)	Product yield (%)
	On anode	On cathode			
3.0-3.2	8.5	15.0	27.7	8.8	81
3.1-3.2	8.0	13.3	25.0	6.2	-

Effect of different additions to the electrolyte. All experiments, the results of which have been given in the tables above, were carried out with technical KOH and K₂CO₃, the composition of which corresponded to the generally recognized standard of these products. In Table 12 are presented the results of a series of experiments aimed at elucidating the effect of some additions to the electrolyte. These experiments also had

the objective of making a comparison of the results obtained when working with technical and chemically pure alkalis. When using chemically pure alkali the current yield rose by 3-4% compared with that when using technical KOH. Use of chemically pure alkali thus increased the product yield by a small amount (2-3%). This is confirmed by the fact that the formation of a slime in the anodic solution of manganese is basically a consequence of the process of incomplete oxidation of manganese on the anode and the reduction of part of the manganate on

the cathode. The formation of a slime at the expense of the reduction of manganate impurities contained in technical alkali does occur to a small extent. The harmful effect of the presence of impurities in the electrolyte, which may be oxidized at the expense of the manganate, was confirmed by experiment. This experiment was carried out by adding a reductant to the electrolyte in the form of Fe^{++} . In this case the manganate formed was used up in oxidizing iron to Fe^{+++} which was reduced again at the cathode. The product of electrolysis was a slime, and there was no manganate in solution. Addition of Cl^- to the electrolyte (in the form of a solution of KCl), in quantity considerably in excess of the usual Cl^- content of technical alkali, did not lower the product yield. Introduction of SO_4^{--} (in the form of K_2SO_4) likewise had no considerable influence on the process of electrolysis. Introduction of NH_4^+ (as ammonium sulfate) lowered the current yield by 6%. These additions had little effect on the product yield. The presence in solution of additional oxidant in the form of potassium dichromate had no influence on the process. The carbonate impurity present in chemical caustic alkali should not have a negative influence on the electrolysis since carbonate solutions appear to have a beneficial influence on the process.

TABLE 12

Effect of additions of electrolyte on the process of anodic solution of manganese in 50% KOH

Quantity of KOH solutions for all experiments 70 ml. Temperature 18°. Potential 3.1 V. Anode c.d. 7.4 A/dm^2 cathode c.d. 22 A/dm^2 .

Electrolyte	Quantity of Mn leaving the anode (g)		Current yield for K_2MnO_4	Product yield (%)
	In solution as K_2MnO_4	In slime		
Technical KOH, 50% solution	0.215	0.028	24.4	89
+5 ml saturated solution KCl	0.241	0.0244	26.7	91
+3 ml saturated solution KCl	0.212	0.018	23.7	92
Chemically pure KOH, 50% solution { +5 ml saturated solution K_2SO_4	0.214	0.016	24.0	93
{ +2 ml saturated solution K_2SO_4	-	-	25.2	-
{ Without additions	0.275	0.018	28.1	93
{ +2 ml saturated solution FeCl_2	Manganate not formed			
Pure KOH, 50% solution	0.154	0.011	28.8	93.3
Technical KOH, 50% solution	0.134	0.012	25.0	91.6
Pure KOH, 50% solution +0.2 ml saturated solution $\text{K}_2\text{Cr}_2\text{O}_7$	0.214	0.015	26.5	93.6
Pure KOH, 50% solution +1 ml saturated solution $(\text{NH}_4)_2\text{SO}_4$	0.119	0.011	22.6	91.5

SUMMARY

1. When using electrolytic metallic manganese as an anode, the passivation of the electrode which had made it impossible to use aluminothermic manganese, ferromanganese, silicomanganese and other widely used manganese alloys, for the production of permanganate was not observed.

2. In the anodic solution of manganese in solutions of K_2CO_3 and in dilute solutions of KOH, permanganate was formed, while in concentrated solutions of KOH, manganate was formed.

3. In the electrolysis of solutions of alkali with a manganese anode, in addition to soluble manganese compounds, there was formed a slime consisting mainly of manganese dioxide. In concentrated solutions the yield both for $KMnO_4$ and for K_2MnO_4 was higher than for manganese dioxide. When the temperature was raised the yield of slime was increased.

4. Use of technical alkali instead of the chemically pure material gave a slightly (3-4%) lower current yield. Iron appears to be a harmful impurity.

5. Optimum conditions of electrolysis for obtaining:

	K_2MnO_4 in KOH solution.	$KMnO_4$ in K_2CO_3 solutions.
Concentration of electrolyte (in g/liter)	Saturated or nearly saturated solution	300-350
Temperature ($^{\circ}C$)	15-20	15-35
Anode c.d. (in A/dm^2)	15-25	3.5-10
Distance between electrodes (in mm)	10	10

6. It is possible to obtain K_2MnO_4 and $KMnO_4$ by anodic solution of electrolytic metallic manganese in KOH and K_2CO_3 solutions (technically pure), with an energy consumption of about 11kwh per kg of product, and using as an anode 80-90% manganese.

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METHOD FOR THE SEPARATE CATALYTIC PREPARATION OF OXYGEN AND CHLORINE FROM $\text{Ca}(\text{ClO})_2$

V. M. Gallak

As long as one hundred years ago calcium hypochlorite was used in many branches of industry, and in spite of extensive literature on it, interest in it has not abated. This is explained above all by the fact that the calcium salt of hypochlorous acid contains a considerable quantity of oxygen and chloride, which can be extracted from it comparatively easily, and also because this substance is a comparatively cheap and easily accessible product which stores well. Calcium hypochlorite is widely used for bleaching cellulose, paper, textiles, etc., for the purification of crude petroleum, for chlorination in industrial chemistry, for degassing, for disinfection, in photography, in laundering, for obtaining chlorine and oxygen, etc.

The various forms in which $\text{Ca}(\text{ClO})_2$ is used in different branches of industry, mainly as a strong oxidant, created the need for a method of intensifying the oxidation processes, with the assistance of various activators and catalysts. Zakoshikov, Nezhelskaya, and Pikhunova [1] proposed a series of activators: hydrogen peroxide, urea, ammonium salts of carbonic, oxalic, and other acids, intensifying the oxidation process by salts of hypochlorous acid. Certain compounds of the metals Ni, Co, Fe, Cu, Mn [2-5a] promote the catalytic decomposition of solutions of calcium hypochlorite, with liberation of oxygen.

The objective of the present work was a detailed study of the catalytic decomposition of calcium hypochlorite, the selection of the most active catalysts, and determination of the optimum conditions for carrying out the given process. We will not dwell upon the chemistry of the oxidizing action of hypochlorite since there is a very extensive literature on this subject [6-8].

EXPERIMENTAL

Production of oxygen. Many catalysts were tried, among which were Co, Fe, Cu, Ni, Mn, and others. Both simple and binary catalysts were examined for their catalytic activity. The catalytic action is exerted by oxides of metals (and not by the metals themselves or their salts, as has been suggested in some papers). Even in those cases where any of the metals indicated above was introduced into calcium hypochlorite to promote its decomposition catalytically, the catalyst was the metal oxide, because in the first stage of the reaction the oxide of the metal was formed at the expense of part of the oxygen of the hypochlorite. In the second stage of the reaction the oxide formed causes the remaining $\text{Ca}(\text{ClO})_2$ to decompose. This observation opened the possibility of preparing any catalyst from compounds of heavy metal, simply, rapidly, and cheaply.

In order that the nature of the catalysts experimented with shall be clear, we will dwell a little on the process of their preparation.

For preparing, for example, a manganese catalyst, 10 g of dry powdered

$\text{Ca}(\text{ClO})_2$ was taken and afterwards a certain quantity of any manganese salt soluble in water, the quantity being such as to contain 0.8 g of metallic manganese. The weighed manganese salt was dissolved in 10 ml of water and $\text{Ca}(\text{ClO})_2$ was added to the solution with stirring. The reaction which occurred may be formulated thus: $\text{Ca}(\text{ClO})_2 + \text{MnCl}_2 \rightarrow \text{MnO}_2 + \text{CaCl}_2 + \text{Cl}_2$. After completion of the reaction the reacting mass was dried, then ground, and the catalyst was ready for use. The majority of the catalysts described below were prepared in this way. (We did not happen accidentally on this method of preparing catalysts. Those which were prepared thus were more active than catalysts from pure metal oxides). The binary catalysts were prepared in exactly the same way. Salts of various metals were taken in the necessary ratio (based on the weight of the metals), in general the quantity taken gave a weight of 0.8 g per 10 g of $\text{Ca}(\text{ClO})_2$. The mixture of salts was treated as in the case of manganese. The catalysts described were mixtures of the metal oxides and calcium salts, the anion of which was in the main the anion of the salt of the heavy metal taken. The majority of the catalysts were prepared from metal chlorides.

Examination of the catalysts for activity was made by comparing the rate and intensity of the catalytic decomposition of $\text{Ca}(\text{ClO})_2$, this being determined by the quantity of oxygen liberated each minute from $\text{Ca}(\text{ClO})_2$: $\text{Ca}(\text{ClO})_2 \rightarrow \text{CaCl}_2 + \text{O}_2$.

The practical evaluation of the activity of a catalyst is illustrated by the following example: 25 g (accurately weighed) of $\text{Ca}(\text{ClO})_2$ ¹ were taken and to it were added 1 g of the catalyst under investigation; after carefully mixing the powders together they were transferred to a round-bottomed flask. After this the mixture of powders was treated with 15 ml of water and the flask closed by a cork with a tube to lead off the gas, the other end of the tube being inserted into a graduated gasometer, filled with water. After the flask was closed it was heated on a boiling water bath and timed with a stop watch. The amount of oxygen collected in the gasometer was noted at the end of each minute. The quantity of oxygen liberated each minute from the $\text{Ca}(\text{ClO})_2$ taken served as a measure of the comparative activity of the catalyst being examined.

A large number of catalysts were examined in this way, including Co, Fe, Cu, Ni, Mn, etc.

Among the single catalysts the best results were shown by cobalt catalysts [9]. The binary catalysts showed greater activity than the single ones. For example, for the very strong pair Co:Fe (Table 1) we show the effect of varying the relative quantities of the components on the activity of the resulting catalysts.

Let us turn our attention to Catalyst No. 43 [11]. This is a cobalt-iron catalyst, in which the weight ratio of the components (calculated as metal) is 3:2. This binary catalyst caused a more rapid and intense initial catalytic decomposition of $\text{Ca}(\text{ClO})_2$ in water, while the reaction continued at a good tempo.

1) The $\text{Ca}(\text{ClO})_2$ with which we worked contained (in %): active chlorine 45.2, CaO (general quantity) 45.02, $\text{Ca}(\text{OH})_2$ (general quantity) 9.56, Cl (general quantity) 30.56, MgO 0.56, $\text{R}_2\text{O}_3(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ 0.3, residue insoluble in HCl, 2.26.

Analysis carried out according to State Standard 1692-46.

TABLE 1

Effect of the composition of the catalyst on its activity

Catalyst No.	Composition of catalyst	Quantity of O ₂ (in ml) liberated per minute							Total O ₂ liberated (in ml)
		Time (in minutes)							
		1	2	3	4	5	6	7	
25	Co	600	1000	500	100	-	-	-	2200
42	Co + Fe (4:1)	625	1125	350	25	-	-	-	2125
43	Co + Fe (3:2)	775	1000	325	100	-	-	-	2200
30	Co + Fe (2.5:2.5) .	600	1025	375	100	-	-	-	2100
44	Co + Fe (2:3)	450	925	500	200	-	-	-	2075
45	Co + Fe (1:4)	250	575	675	300	200	100	-	2100
46	Fe	65	85	100	150	125	50	50	625

Since Catalyst No. 43 was more active than many of the catalysts investigated, it was decided to make a more detailed study of its basic properties. We carried out a series of experiments to study the effect of the quantity of catalyst on the rate of decomposition of $\text{Ca}(\text{ClO})_2$.

In Table 2 are set forth the results of experiments which confirm the direct dependance between the quantity of catalyst and the rate of reaction. The table can be of practical use to indicate the amount of catalyst that must be taken in order to get the desired rate of liberation of gas from $\text{Ca}(\text{ClO})_2$ by catalytic decomposition.

To study the effect of temperature on the rate of catalytic decomposition of $\text{Ca}(\text{ClO})_2$ a series of experiments was carried out at temperatures of 20-100° in which 1 or 2 g of catalyst were mixed with 25 g of $\text{Ca}(\text{ClO})_2$. The results of these experiments can be seen in Table 3.

This table can also be utilized for selection of the conditions under which the decomposition of $\text{Ca}(\text{ClO})_2$ should be conducted in order to get the necessary (specified) rate of reaction. It should be mentioned here that for intensification of oxidation with $\text{Ca}(\text{ClO})_2$ it is necessary to use a small quantity of the catalyst described at comparatively low temperatures; whereas to get oxygen a large quantity of catalyst at a higher temperature should be utilized. The necessary conditions can be selected with the aid of Tables 2 and 3.

We studied separately the stability of mixtures of $\text{Ca}(\text{ClO})_2$ and the catalyst on storage. If $\text{Ca}(\text{ClO})_2$ and Catalyst No. 43 are dried separately at 80-90° and afterwards mixed, then this mixture is completely stable and can be stored practically for years without change. Only access of moisture to this mixture can cause a catalytic decomposition of the $\text{Ca}(\text{ClO})_2$. When working with the catalyst described, the question naturally arises as to what would be the catalytic activity of pure oxides of metals and of their mixtures.

It can be said immediately that catalysts of pure metal oxides are inferior in activity to the catalytic mixtures. The excellence of the catalytic activity of the mixtures may be explained by the fact that low-solubility compounds of calcium, such as carbonate, hydroxide and other minerals act as supports for the catalysts, and this is reflected positively in their activity. The support facilitates an increase in the dispersion of the catalyst itself, by increasing its active surface.

When all the basic questions connected with the properties and behavior of the catalysts studied had been clarified, it appeared desirable to return to the question of the temperature of the reaction of the catalytic decomposition of $\text{Ca}(\text{ClO})_2$.

TABLE 2

Effects of quantity of catalysts on the rate of reactions

Quantity of catalyst (in g)	Quantity of O ₂ (in ml) liberated per minute													Total O ₂ liberated (in ml)
	Time (in minutes)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	
0.0	Liberation of O ₂ weak (20-25 ml per minute)													
0.2	250	300	450	350	200	200	100	100	75	75	50	50	50	2250
0.4	300	700	550	325	200	75	50	-	-	-	-	-	-	2200
0.6	450	850	650	175	75	-	-	-	-	-	-	-	-	2200
0.8	600	1050	450	100	30	-	-	-	-	-	-	-	-	2230
1.0	750	1000	350	100	-	-	-	-	-	-	-	-	-	2200
1.2	875	975	250	25	-	-	-	-	-	-	-	-	-	2125
1.4	1000	975	125	-	-	-	-	-	-	-	-	-	-	2100
1.6	1200	800	175	-	-	-	-	-	-	-	-	-	-	2175
1.8	1250	850	75	-	-	-	-	-	-	-	-	-	-	2175
2.0	1300	825	125	-	-	-	-	-	-	-	-	-	-	2250
2.2	1400	725	100	-	-	-	-	-	-	-	-	-	-	2225
2.4	1450	750	50	-	-	-	-	-	-	-	-	-	-	2250
2.6	1550	650	25	-	-	-	-	-	-	-	-	-	-	2225
2.8	1650	550	25	-	-	-	-	-	-	-	-	-	-	2225
3.0	1700	425	100	-	-	-	-	-	-	-	-	-	-	2225
3.5	1750	450	50	-	-	-	-	-	-	-	-	-	-	2250
4.0	1850	350	25	-	-	-	-	-	-	-	-	-	-	2225
4.5	1750	400	50	-	-	-	-	-	-	-	-	-	-	2200
5.0	1600	525	25	-	-	-	-	-	-	-	-	-	-	2150

TABLE 3

Effect of temperature on the rate of decomposition of Ca(ClO)₂

Temp. of Expt. (°C)	Quantity of catalyst (in g)	Quantity of O ₂ (in ml) liberated per minute												Total O ₂ liberated (in ml)	Remarks
		Time (in minutes)													
		1	2	3	4	5	6	7	8	9	10	11	12		
20	1	22	22	22	22	22	22	23	23	23	23	23	23	270	Liberation of O ₂ continued
	2	100	100	100	100	100	100	95	95	95	95	95	95	1170	
30	1	70	70	70	70	70	70	70	70	70	70	75	75	850	
	2	100	150	250	250	250	150	100	100	75	75	25	25	1550	
40	1	70	75	85	130	150	200	200	200	200	70	60	60	1500	
	2	200	270	430	400	250	100	75	20	15	15	15	10	1800	
50	1	130	170	250	425	400	225	125	75	50	50	25	25	1950	
	2	250	400	850	250	75	50	40	35	25	25	15	10	2025	
60	1	175	200	375	600	325	150	75	50	50	15	5	5	2025	
	2	375	750	750	150	40	25	20	5	5	5	-	-	2125	
70	1	250	375	650	525	225	50	25	15	5	5	-	-	2125	
	2	450	1050	575	75	25	-	-	-	-	-	-	-	2175	
80	1	300	700	650	275	100	-	-	-	-	-	-	-	2225	
	2	500	1250	475	25	-	-	-	-	-	-	-	-	2250	
90	1	400	700	650	275	50	-	-	-	-	-	-	-	2275	
	2	650	1100	450	50	-	-	-	-	-	-	-	-	2250	
100	1	700	1000	500	50	-	-	-	-	-	-	-	-	2250	
	2	1000	1200	100	-	-	-	-	-	-	-	-	-	2300	

It was interesting to see if it were possible to conduct this process without the use of external heat at the same intensity as when it was heated. For this we used the well known exothermal reaction - the slaking of lime: $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 16 \text{ kcal [10]}$.

As this reaction is completely compatible with the basic reaction, neither of them affecting the progress of the other we considered it was possible to conduct a series of experiments on self-heating reaction mixtures with the help of the reactions mentioned.

In these experiments 25 g of $\text{Ca}(\text{ClO})_2$ was taken, 1 g of Catalyst No. 43 and a weighed amount of CaO, commencing with 1 g and ending with 40 g (grain size of CaO up to 1 mm). It was established empirically that besides the usual 15 ml of water it was necessary to add 1 ml of water for every 1 g of CaO (this is considerably larger than the stoichiometric quantity). These experiments, like all the remaining ones, were conducted with a thermometer inserted into the reaction mass, and each minute there was noted the volume of oxygen liberated (numerator in table), and the temperature in the reaction mass (denominator in table). The results of these experiments are collected in Table 4.

As can be seen from Table 4, the highest temperature was developed in experiments with $\text{Ca}(\text{ClO})_2/\text{CaO}$ (ratio of 1:1 per 25 g). A glance at the table shows that the amount of oxygen liberated by the calcium hypochlorite considerably increases in sequence with the experiments. In all previous experiments the quantity of oxygen was equal to around 2,200 ml, when heated externally. In these experiments this quantity began to increase and in the later experiments we got a yield of 2,510 ml of oxygen. We can explain this by the deeper heating of each particle of reaction mixture - deeper than when heating the flask externally. It is evident that a definite role is played here in that the last three experiments were carried out with CaO, the size of the grains of which was equal to 1 - 3 mm and such a calcium oxide keeps better and longer than a powdery one.

It can be seen from the table that in experiments with external heating the initial stage of the reaction is more intense than when heating with lime. This initial sluggishness of the process may be eliminated if a small quantity of sodium peroxide is added to the charge. The latter reacts energetically and exothermally with water, and gives a thermal impulse to the basic reaction. A simpler means of overcoming the initial slowness of the reaction can be used, namely: adding pre-heated water to the reaction mixture. This simple but radical means permits the more intensive production of oxygen from the very start of the reaction.

In order to complete that part of the experiments which relate to the production of oxygen we prepared a reactive mixture of average activity (Table 4, Experiment 6) in order to study the fall of its activity with time.

The composition of the mixture was as follows: 1) $\text{Ca}(\text{ClO})_2$ (dried at 80-90° for 5 hours) - 150 g; 2) CaO (grain size up to 1 mm) - 120 g; 3) catalyst - 6 g.

After careful mixing, the prepared mixture was transferred to a clear glass bottle with a ground stopper, and stored in diffused daylight at an air temperature of 20-25°. In the course of the first three months the mixture was examined every month, and subsequently once each year. For each test 46 g of mixture (its composition: 25 g $\text{Ca}(\text{ClO})_2$ + 20 g CaO + 1 g catalyst) and 35 ml water were taken.

TABLE 4

Temperature regime of the reaction of catalytic decomposition of $\text{Ca}(\text{ClO})_2$

Quantities of $\text{Ca}(\text{ClO})_2$ and CaO (in g)	Quantity of O_2 (in ml) liberated per minute (in numerator) and temperature of mixture (in degrees) at each minute (in denominator)												
	Time in minutes												
	1	2	3	4	5	6	7	8	9	10	11	12	13
25+1	$\frac{30}{27}$	$\frac{40}{31}$	$\frac{50}{33}$	$\frac{60}{35}$	$\frac{70}{39}$	$\frac{80}{43}$	$\frac{90}{47}$	$\frac{100}{51}$	$\frac{125}{55}$	$\frac{145}{59}$	$\frac{190}{62}$	$\frac{170}{64}$	$\frac{160}{66}$
25+3	$\frac{30}{29}$	$\frac{40}{33}$	$\frac{50}{36}$	$\frac{65}{40}$	$\frac{85}{45}$	$\frac{100}{50}$	$\frac{130}{56}$	$\frac{140}{61}$	$\frac{160}{66}$	$\frac{170}{70}$	$\frac{200}{74}$	$\frac{150}{76}$	$\frac{120}{77}$
25+5	$\frac{55}{35}$	$\frac{95}{41}$	$\frac{150}{50}$	$\frac{200}{59}$	$\frac{240}{72}$	$\frac{250}{81}$	$\frac{210}{84}$	$\frac{180}{86}$	$\frac{150}{86}$	$\frac{100}{85}$	$\frac{80}{83}$	$\frac{60}{81}$	$\frac{50}{79}$
25+10	$\frac{55}{37}$	$\frac{95}{46}$	$\frac{170}{55}$	$\frac{230}{67}$	$\frac{250}{76}$	$\frac{210}{81}$	$\frac{200}{84}$	$\frac{180}{86}$	$\frac{160}{88}$	$\frac{150}{89}$	$\frac{100}{90}$	$\frac{70}{89}$	$\frac{50}{88}$
25+15	$\frac{60}{39}$	$\frac{100}{49}$	$\frac{170}{60}$	$\frac{210}{72}$	$\frac{220}{79}$	$\frac{230}{84}$	$\frac{240}{89}$	$\frac{270}{95}$	$\frac{260}{99}$	$\frac{220}{100}$	$\frac{90}{101}$	$\frac{45}{100}$	$\frac{20}{99}$
25+20	$\frac{50}{38}$	$\frac{100}{47}$	$\frac{160}{57}$	$\frac{200}{68}$	$\frac{240}{78}$	$\frac{280}{88}$	$\frac{400}{97}$	$\frac{360}{101}$	$\frac{270}{103}$	$\frac{145}{104}$	$\frac{50}{104}$	$\frac{20}{103}$	—
25+25	$\frac{60}{42}$	$\frac{120}{58}$	$\frac{180}{69}$	$\frac{220}{78}$	$\frac{350}{88}$	$\frac{420}{99}$	$\frac{400}{105}$	$\frac{230}{107}$	$\frac{120}{107}$	$\frac{80}{107}$	$\frac{20}{105}$	—	—
25+30	$\frac{25}{31}$	$\frac{50}{36}$	$\frac{75}{46}$	$\frac{100}{57}$	$\frac{220}{68}$	$\frac{400}{78}$	$\frac{700}{99}$	$\frac{500}{101}$	$\frac{300}{101}$	$\frac{110}{100}$	—	—	—
25+35	$\frac{20}{29}$	$\frac{45}{34}$	$\frac{65}{41}$	$\frac{85}{48}$	$\frac{135}{56}$	$\frac{260}{65}$	$\frac{500}{90}$	$\frac{700}{98}$	$\frac{450}{102}$	$\frac{200}{103}$	$\frac{40}{102}$	—	—
25+40	$\frac{20}{29}$	$\frac{30}{34}$	$\frac{45}{43}$	$\frac{65}{52}$	$\frac{100}{62}$	$\frac{200}{73}$	$\frac{380}{83}$	$\frac{700}{98}$	$\frac{600}{101}$	$\frac{280}{102}$	$\frac{60}{101}$	$\frac{30}{100}$	—

It should be mentioned that on prolonged drying of $\text{Ca}(\text{ClO})_2$ the quantity of active chlorine fell, for example to 36%.

The results of the checking experiments, which extended over 2 years, are shown in Table 5.

As is evident from Table 5, the mixture for the production of oxygen was extremely stable. The quantity of oxygen liberated scarcely changed in the course of 2 years (within the limits of experimental error).

For the practical utilization of the oxygen-generating mixture it is convenient to prepare it in the form of tablets, by pressing or briquetting. For briquetting, the powder mixture was wetted with a solution of colophony in very dry dichloroethane, the briquettes were formed and subsequently dried without exposure to carbon dioxide or water vapor.

Production of chlorine. In the chemical literature, particularly in the patent literature, many methods for obtaining chlorine from chloride of lime

TABLE 4

Temperature regime of the reaction of catalytic decomposition of $\text{Ca}(\text{ClO})_2$ Quantity of O_2 (in ml) liberated per minute (in numerator) and temperature of mixture (in degrees) at each minute (in denominator)Total O_2 liberated (in ml)

Time in minutes								
14	15	16	17	18	19	20	21	
$\frac{130}{68}$	$\frac{120}{68}$	$\frac{100}{68}$	$\frac{60}{67}$	$\frac{40}{66}$	$\frac{25}{64}$	$\frac{10}{63}$	$\frac{5}{61}$	1800
$\frac{100}{78}$	$\frac{80}{78}$	$\frac{70}{76}$	$\frac{60}{75}$	$\frac{40}{73}$	$\frac{20}{71}$	$\frac{10}{69}$	$\frac{5}{67}$	1825
$\frac{40}{77}$	$\frac{35}{74}$	$\frac{30}{72}$	$\frac{25}{70}$	$\frac{20}{68}$	$\frac{15}{66}$	$\frac{10}{63}$	$\frac{5}{62}$	2000
$\frac{40}{86}$	$\frac{35}{85}$	$\frac{30}{82}$	$\frac{25}{80}$	$\frac{20}{77}$	$\frac{15}{74}$	$\frac{10}{72}$	$\frac{5}{70}$	2100
—	—	—	—	—	—	—	—	2135
—	—	—	—	—	—	—	—	2275
—	—	—	—	—	—	—	—	2200
—	—	—	—	—	—	—	—	2480
—	—	—	—	—	—	—	—	2500
—	—	—	—	—	—	—	—	2510

and calcium hypochlorite are encountered.

Winkler's method is most worthy of mention [5b].

We observed that in the catalytic decomposition of $\text{Ca}(\text{ClO})_2$ in water only oxygen was liberated, but when $\text{Ca}(\text{ClO})_2$ was heated in the presence of these catalysts it decomposed with liberation of chlorine. The production of chlorine by the catalytic decomposition of $\text{Ca}(\text{ClO})_2$ is even simpler than that of oxygen.

Take, for example, 25 g of dry $\text{Ca}(\text{ClO})_2$ and add to it 1 g of Catalyst No. 43. After mixing the powders, transfer them to a round-bottomed flask, and close it with a cork carrying a gas-outlet tube. The gas is collected over a saturated aqueous solution of salt. The flask is placed on a sand bath or an electric hot plate covered with asbestos. On heating the flask, for example to 60° , chlorine begins to be liberated. This liberation proceeds with great vigor; and therefore, as soon as gas begins to come off the plate should be switched off. The bulk of the chlorine is liberated between 60 - 70° . When the rate of generation of gas begins to slacken, the hot plate may be switched on

TABLE 5

Results of experiments to confirm the stability of the reaction mixture on long storage

Expt. No.	Temperature of water (in deg.)	Date of experiment	Quantity of O ₂ (in ml) liberated per minute (numerator) and temperature of reaction liquid for every minute of reaction (in deg.) (denominator)							
			Time (in min)							
			1	2	3	4	5	6	7	
1	19	4/14/1947	$\frac{200}{60}$	$\frac{270}{76}$	$\frac{320}{87}$	$\frac{370}{97}$	$\frac{470}{103}$	$\frac{420}{107}$	$\frac{120}{107.5}$	
2	21	5/14/1947	$\frac{150}{57}$	$\frac{200}{74}$	$\frac{275}{85}$	$\frac{325}{92}$	$\frac{350}{99}$	$\frac{450}{105}$	$\frac{250}{107}$	
3	22	6/14/1947	$\frac{150}{60}$	$\frac{225}{77}$	$\frac{300}{88}$	$\frac{325}{95}$	$\frac{450}{102}$	$\frac{300}{106}$	$\frac{250}{107}$	
4	27	7/17/1947	$\frac{200}{70}$	$\frac{350}{86}$	$\frac{400}{94}$	$\frac{425}{101}$	$\frac{400}{105}$	$\frac{225}{107}$	$\frac{75}{107}$	
5	23	4/14/1948	$\frac{80}{31}$	$\frac{100}{39}$	$\frac{140}{48}$	$\frac{260}{59}$	$\frac{280}{74}$	$\frac{300}{89}$	$\frac{360}{95}$	
6	21	4/14/1949	$\frac{50}{32}$	$\frac{70}{39}$	$\frac{100}{48}$	$\frac{120}{56}$	$\frac{130}{65}$	$\frac{160}{71}$	$\frac{170}{79}$	

again and the residual chlorine liberated by heating the reaction mass to 120°. The quantity of chlorine liberated is the same as that of oxygen in the earlier-described experiments (for the same weight). Chlorine obtained in the manner described contains a small quantity of oxygen as an impurity.

The decomposition of $\text{Ca}(\text{ClO})_2$ involving the liberation of chlorine is considerably accelerated both by the copper-cobalt catalyst, and also by an iron-cobalt one, however, with a smaller cobalt content ($\text{Co:Fe} = 1:4$).

From the experimental results we see that either oxygen or chlorine may be obtained from $\text{Ca}(\text{ClO})_2$, depending on the conditions and using one or another of the catalysts.

SUMMARY

1. The possibility of catalytic activation of the process of oxidation by hypochlorites with the aid of small quantities of catalyst at low temperatures, and also the production of oxygen by using large quantities of catalyst at higher temperatures, has been demonstrated.
2. It has been shown that $\text{Ca}(\text{ClO})_2$ and oxides of some heavy metals (catalysts) are completely passive to one another when stored together in the dry state.
3. It has been confirmed that the catalysts are not salts of the heavy metals, but oxides of these metals.
4. The method indicated can replace the difficultly available KClO_3 (for obtaining oxygen) and the mixture of manganese dioxide and HCl (for obtaining chlorine) by the cheaper and more easily available $\text{Ca}(\text{ClO})_2$.

TABLE 5

Results of experiments to confirm the stability of the reaction mixture on long storage

Quantity of O ₂ (in ml) liberated per minute (numerator) and temperature of reaction liquid for every minute of reaction (in deg.) (denom- inator)								Total O ₂ liberated (in ml)
Time (in min)								
8	9	10	11	12	13	14	15	
$\frac{60}{107.5}$	$\frac{20}{107}$	-	-	-	-	-	-	2250
$\frac{60}{107}$	$\frac{40}{107}$	$\frac{25}{106}$	-	-	-	-	-	2125
$\frac{65}{108}$	$\frac{40}{107}$	$\frac{20}{106}$	-	-	-	-	-	2125
$\frac{50}{107}$	$\frac{15}{105}$	-	-	-	-	-	-	2140
$\frac{320}{97}$	$\frac{250}{98}$	$\frac{50}{99}$	$\frac{32}{99}$	$\frac{25}{98}$	-	-	-	2200
$\frac{200}{86}$	$\frac{250}{91}$	$\frac{250}{94}$	$\frac{300}{97}$	$\frac{200}{97}$	$\frac{80}{97.5}$	$\frac{50}{97}$	$\frac{20}{96}$	2150

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GRAPHICAL METHOD OF CALCULATING SYSTEMS OF CONTINUOUS ACTION APPARATUS FOR LIQUID PHASE REACTIONS

I. V. Provinteev

In recent years apparatus and systems of apparatus for conducting reactions continuously have achieved wide use in modern industry for the realization of organic syntheses.

For a number of similar processes continuous reactors were introduced some 10 years ago for reactions in the liquid phase. The absence of a method of calculating such apparatus led, until quite recently, to their design by copying existing apparatus and to some purely empirical improvements of them.

In recent years the Soviet scientists Planovsky [1] and Kirillov [2,3] worked out a basis for calculating individual cases of continuous reactors. In the present work the objective is to extend the work of the above two authors in the field of calculation of continuous reactors, and to permit the use of a graphical calculation of a general type of apparatus in which to carry out any reaction.

In any reactor with a stirrer the latter serves for the mixing of the reaction mixture and for the creation of a definite circulation in the apparatus; in this mixing the reacting components come under the action of: 1) differential velocity of movement of the surfaces undergoing circulation and the reacting liquid; and 2) differences in rate of movement of separate layers of liquid along all the circulation contours.

Depending upon the construction of the mixer, the circulation of the reaction mixture in the apparatus will have a different character. The characteristics of the circulation of the reaction mixture inside the apparatus may be divided into three groups.

1. Apparatus with ideal circulation. In this apparatus any particle of the reaction mixture follows one and the same circulation contour, i.e. the period of residence of each particle in the apparatus, from the moment of rejection by the mixer to the moment of becoming entrained again, is the same (identical period of reaction) (Fig. 1).

2. Apparatus with normal circulation. In this apparatus each portion of reaction mixture has its own special circulation contour passing through the mixing zone, and the period of reaction of one portion is not equal to the period of reaction of another portion.

Each portion, proceeding along its own circulation contour, passing repeatedly into the mixer, has its own degree of completion of the reaction, differing from the degree of completion of the reaction in neighboring portions. The general degree of completion of the reaction in this apparatus (periodic action) may be expressed thus:

$$X_0 - X_k = \sum_{i=1}^m \sum_{j=1}^n \Delta(X_0^i - X_k^j), \quad (1)$$

where: m is the number of portions having individual periods of circulation; n is the number of the periods of circulation of each portion; $\Delta(x_0^1 - x_k^1)$ is the degree of completion of the reaction for one portion in one period of circulation.

Consequently this apparatus can be looked on as an apparatus with ideal circulation, taking an average value for $X_0 - X_k$ (Fig. 2).

3. Apparatus involving closed circulation. In this apparatus some of the particles do not fall into the mixing zone and are not rejected by it and, at the expense of the kinetic energy of the particles, move as a rule, in a closed circulation contour (dead space) (Fig. 3). Such a phenomenon is very undesirable in apparatus involving reaction processes, especially reactions in which there is a danger of explosion.

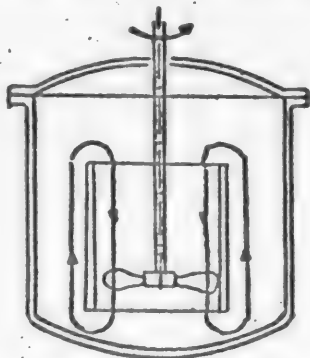


Fig. 1. Apparatus with ideal circulation.

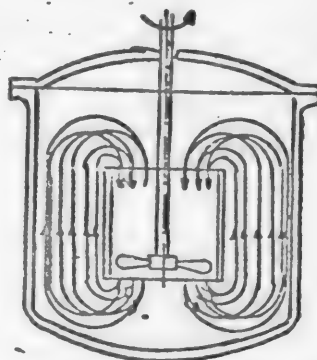


Fig. 2. Apparatus with normal circulation.

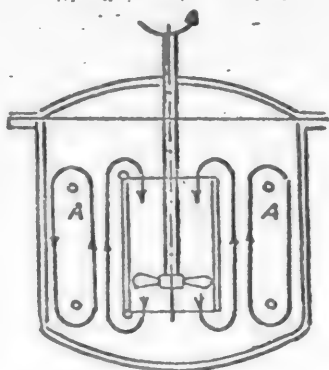


Fig. 3. Apparatus with double circulation. A = dead zone.

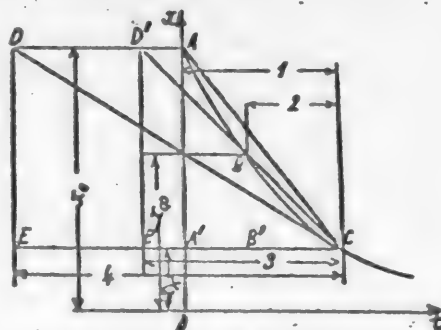


Fig. 4. Calculation of apparatus for continuous action. $\Delta CAA' Q = V_0 = \max V$; $\Delta CD' E' Q > V$; 1 - $t_0 = \frac{V_a}{V_0}$; 2 - $t_c = \frac{V_a}{Q}$; 3 - $t_r = \frac{V_a}{V}$; 4 - $t_m = \frac{V_a}{V} \min$.

For the determination of conditions under which continuous reactions should be carried out, we assume the condition that the apparatus being analyzed works in the first or second group with an average value of concentration in the apparatus. When continuous processes of reaction are carried out in apparatus the following phenomena occur.

Inside the apparatus the initial component continuously enters the mixer with

an initial concentration X_0 in quantity $V \text{ m}^3/\text{hr}$, and a quantity $V \text{ m}^3/\text{hr}$ leaves the apparatus at the concentration X_k . The reacted liquid also returns to the mixer at a concentration X_k and quantity $Q - V \text{ m}^3/\text{hr}$ where Q = capacity of the circulation impeller (stirrer) in the apparatus. Different quantities of liquids with different concentrations are mixed.

The average concentration of the mixture at the moment when mixing starts may be determined from the mixing equation, i.e.:

$$X_{av.} = \frac{VX_0 + (Q - V) X_k}{Q} \quad (2)$$

If the working volume of the apparatus is equal to $V_a \text{ m}^3$, the ration V/Q may be deduced as follows.

Dividing and multiplying V/Q by the volume of the apparatus V_a the ratio V_a/Q will be determined by the average period of circulation of the mixture in the apparatus t_c , and the ratio V_a/V will be determined by the average time of residence of the mixture in the apparatus t_{av} . In this case equation 2 takes the form:

$$X_{av.} = \frac{t_c}{t_r} X_0 + (1 - \frac{t_c}{t_r}) X_k \quad (2')$$

I. Calculations of continuous acting apparatus

It follows from Equation (2') that the fall of concentration is quite directly proportional to the ratio V/Q or t_c/t_r , i.e. the dependence is determined by similar triangles. On the other hand the plot of $t-X$ for all reactions, excluding those of zero order, is a curve. The simultaneous solution of these two conditions permits the calculation, graphically, both of continuous acting apparatus and also systems of such reactors. This can be done as follows:

Let us assume that we have the graph $t-X$ for any process of reaction (Fig. 4), and also that the capacity of the apparatus is specified along with the initial and final concentration of products, the specific generation of heat and the temperature of the process in the apparatus. It is required to determine: the volume of the apparatus, the concentration of the mixture in process of reaction in the apparatus, and its relative coefficient of useful work.¹

1. Determine from the conditions of heat balance the output of the mixer $Q \text{ m}^3/\text{hr}$.
2. Determine the average concentration of the mixture in the apparatus from Equation (2').
3. Lay off $X_{av.}$ on the ordinate axis and draw a horizontal line to intersect the $t-X$ curve. The point of intersection will be the point which indicates the concentration of the mixture in the apparatus. The intercept $C-B'$ gives the period of reaction. From here we determine the required volume of the apparatus, i.e.;

$$V_a = Qt_c.$$

The intercept $B-C$ of the curve is the working portion of the curve along which the process of reaction produces a fall in concentration. The intercept $A-B$ represents the loss in concentration.

¹) In the rest of this paper this coefficient of useful work of the apparatus is shortened to CUW.

Draw a straight line through the points D and C to intersection with the horizontal drawn through the point A. From the construction it is seen that the line D'-E' is the complete fall of concentration $X_0 - X_k$. Consequently the intercept C-E' should, according to Equation (2'), be the quantity $t_{av.} = V_a/V$. By this means we can confirm the correctness of our construction since the value V obtained from the graph should correspond with the value V assumed by us.

Variation in $X_{av.}$ changes the inclination of the line C-B-D. The magnitude $t_{av.}$, inversely proportional to the output of the apparatus, increases with decreasing $X_{av.}$ and it decreases with increasing $X_{av.}$

With increasing output of the stirrer, the value $t_c = V_a/Q$ will decrease. Consequently the points of intersection (C and B) of the line C-B-D with the curve A-B-C will be near to one another. Under the condition of ensuring the final concentration X_k the point B becomes very near to the point C and the intersection of the lines C-B-D with the line A-D is displaced towards the left, and the intercepts C-E' determined by the value $t_{av.}$ and V, will increase. Consequently, the time of residence $t_{av.}$ will likewise increase, and the output of the apparatus, V, will diminish.

Thus with increase in Q the value $X_{av.}$ will diminish: together with this the output of the apparatus will also diminish and for $Q \rightarrow \infty$ the output of the apparatus will approach a minimum. In this case the line C-B-D coincides with the line tangent to the curve at the point C.

This conclusion is in complete agreement with the analytical conclusions from the concentration equation for reaction processes in apparatus, which indicate that with increase of Q to ∞ , the concentration of the mixture approximates the final concentration, i.e. $X_{av.} \rightarrow X_k$, and the output of the apparatus approaches a minimum (Fig. 4).

With increase of the value $X_{av.}$ the output of the apparatus will increase and approach its maximum value at the moment when $X_{av.}$ agrees with the value X_0 , i.e. when the quantity of circulating liquid in the apparatus is zero and the apparatus is thereby converted to one of ideal circulation.

Consequently and reciprocally it is necessary to introduce such a quantity as will guarantee the stability of the temperature of the process of reaction in the apparatus at a definite level.

The larger increase in quantity of recirculating liquids under conditions which secure complete mixing in the mixing zone results in a diminished output of the apparatus.

Finally setting the condition that the given apparatus has a definite construction of the circulation impeller and consequently a definite output, the reaction constant for the definite reaction carried out at a definite temperature under nearly constant conditions is constant. The effect of construction of the perfect apparatus is determined by its comparative constructional CUW.

In the given case the question of the influence of limiting the flow of reaction mass in the apparatus on its output is discussed.

It is natural to suppose that lowering the quantity of recirculating liquid leads to a diminished rate of movement along the circulation contour, which in its turn negatively affects the reaction constant, but in the case in point this effect is easily avoided by some means, namely: when lowering the output of the circulation impeller, the cross-sectional area of the circulation contour must be correspondingly diminished so that the rate of movement of the reaction mass can remain as before,

which permits the maintenance of the reaction constant at the previous level; 2) by increasing the dispersive power of the circulation impeller, a lowering of the dispersive power of the reaction mass, due to a lowering of the rate of its movement on the circulation contour, can be compensated.

In the design of new reaction apparatus it is necessary to aim at such a construction as will give the maximum degree of dispersion at the expense of the rate of flow and at the same time to get the output of the impeller to be that corresponding to the specified conditions.

In this case these two factors not only do not contradict one another but both exert a positive effect on the output of the apparatus.

II. Graphical calculation of systems of continuous reactors

In many cases when carrying out reactions in continuous systems it is more advantageous, both from the point of view of the conduct of the process, and from the point of view of its economic realization, to use instead of one continuous reactor a system of several such reactors joined in series. In this case the fresh initial component enters the main (first) apparatus, after which the partially reacted mixture enters the next apparatus where it reacts further, and then the mixture goes through another apparatus and so on until such time as the required concentration X_k of the initial products in the reaction products is attained (Fig. 5).

Using the above described graphical analytical method of calculation for continuous reactors we can also calculate systems comprising m individual continuous reactors.

Let us suppose that it is necessary to calculate a system of reactors, and suppose that for this purpose we have graphs of periodic processes in reactors of analogous construction, and that the number of reactors, the output of the system, or the size of each reactor, are known.

It is necessary to calculate the volumes of the apparatus or the output of the system, and likewise the relative CUW of the system.

The calculation may be made in two ways: 1) for equal volumes of the apparatus (reactors) and 2) for equal falls of concentration.

In both cases the calculation may be made either for optimum or for minimum output, i.e., in the first case - to get an increase of the relative CUW of the apparatus - the output of the mixer is calculated for conditions of thermal balance, and the line C-B-D is a secant of the curve of the process $t-X$ cutting it in two points, the difference in the abscissae of which is the ratio V_a/Q ; in the second case, for which it is required that the quantity of circulating liquid ($Q-V$) shall be large, the calculation may be carried out for minimum output, i.e., for the case of ideal circulation.

Calculation for equal volumes of reactors. (a) Calculation for minimum output (Fig. 6.) On the intercept of the curve $t-X$, representing the fall of concentration in the reaction from X_0 to X_k , let us construct a number of right-angled triangles equal to the number of the reactors, of which the hypotenuses C_1-D_1 will be tangents to the $t-X$ curves at the points C_1 , the adjacent sides C_1-E_1 should be equal, in view of the imposed condition of the equality of volumes and identity of the separate outputs. The adjacent sides E_1-D_1 represent the falls

in concentration $X_0^c - X_k^1$ in the reactors.

From the condition that the intercepts $C_1-E_1 = Va/V$, we determine the unknown volumes of the apparatus or their outputs. The C_1 points give the value of the concentration of the mixture.

b) Calculation of a system for the optimum regime. If, in the determination of the quantity of recirculating liquid according to the thermal balance, the amount comes out to be commensurate with the output of the reactors, then for the increase of the output of the reactors or a decrease in the specified volume of the system of reactors, the output of the mixers must be calculated from the output specified for each reactor.

In this case the graph for the calculation will have the following form (Fig. 7).

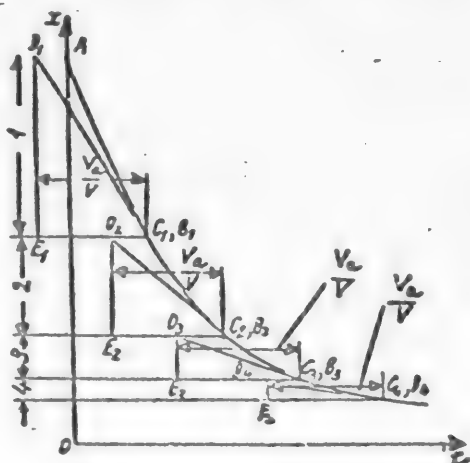


Fig. 6. Calculation of systems of reactors for minimum output.

$$Q = \infty; \frac{V_0^m}{V} = \text{const}; 1 - X_0 - X_p^I;$$

$$2 - X_p^I - X_p^{II}; 3 - X_p^{II} - X_p^{III}; 4 - X_p^{III} - X_k.$$

The points C_1 would then characterize the final concentration in each apparatus. From each point C_1 , lay off towards the left the lines C_1-E_1 determining the ratio V_{a1}/Q . The ordinate drawn from the point E_1 to its intersection with the curve at the point B_1 gives the corresponding value for the concentration of the mixture. The intercepts of the ordinates D_1-F_1 give the value of the fall of concentration for each apparatus. The volumes of the apparatus or their outputs are determined in a manner analogous to the previous example.

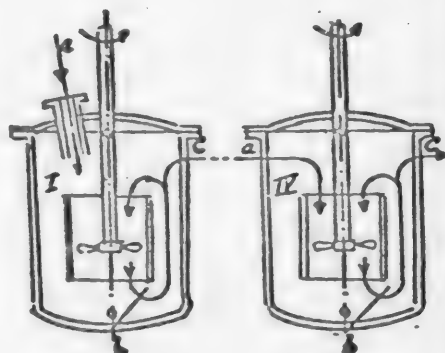


Fig. 5. Liquid flow lines in a system of reactors.

1 - apparatus $g_1 \frac{M^3}{\text{hr}}$:

$$a - V \frac{M^3}{\text{hr}}, X_0 \%, \sum_1^n n \text{ const};$$

$$b - \frac{Q_1 \frac{M^3}{\text{hr}} X_0^1 \%}{t_r^I \text{ } ^\circ\text{C}}; c - V \frac{M^3}{\text{hr}},$$

$$X_k^I, t_{\text{intermed}}^I.$$

IV - apparatus $g_4 = g_1 \frac{M^3}{\text{hr}}$:

$$a - V \frac{M^3}{\text{hr}}, X_k^{III}, t_{\text{intermed}}^{I \text{ II}}$$

$$b - \frac{Q \frac{M^3}{\text{hr}}, X_0^{IV} \%}{t_r^{IV} \text{ } ^\circ\text{C}}; c - V \frac{M^3}{\text{hr}},$$

$$X_k^{IV}, t_{\text{intermed}}^{IV}.$$

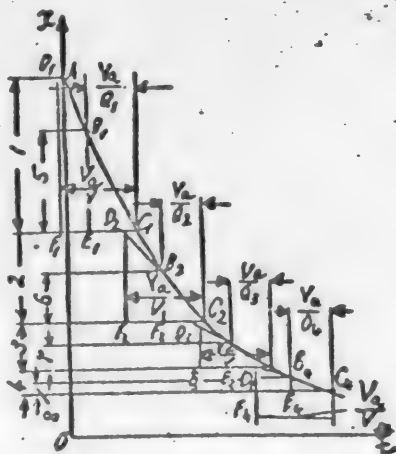


Fig. 7. Calculation of systems of reactors for optimum output.

$$Q = f(x_p^m - x_k^m); \quad \frac{V^m}{a} = \text{const}; \quad 1 - x_0 - x_k^I;$$

$$2 - x_k^I - x_k^{II}; \quad 3 - x_k^{II} - x_k^{III};$$

$$4 - x_k^{III} - x_k^{IV}; \quad 5 - x_p^I - x_k^I; \quad 6 - x_p^{II} - x_k^{II};$$

$$7 - x_p^{III} - x_k^{III}; \quad 8 - x_p^{IV} - x_k^{IV}.$$

Calculation for equal fall of concentration. a) Calculation for minimum output. In this case the total fall of concentration specified is divided into a number of equal falls in each separate reactor.

From the points C_1 (Fig. 8) draw a tangent C_1-D_1 to the intersection with the corresponding line for the initial concentration. The section of the abscissa C_1-E_1 gives the value of the ratio V_{a1}/V . Consequently, the volume of the apparatus may be determined from this, i.e.;

$$V_{a1} = V \cdot \text{intercept. } C_1 - E_1; \quad V_{a2} = V \cdot$$

intercept. $C_2 - E_2$ etc.

In this case, as can be seen from the graphical construction, it follows that, when the concentration is lowered, the volume of the apparatus increases. A specially large volume is obtained for the last reactor.

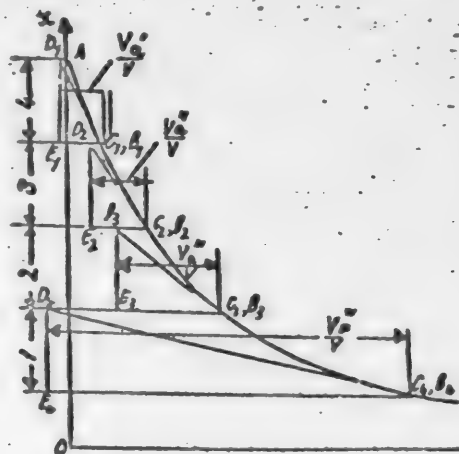


Fig. 8. Calculation for equal fall of concentration for minimum output.

$$Q = \infty; \quad m = \text{number of reactors.}$$

$$1, 2, 3 \text{ and } 4 - \frac{x_0 - x_k}{m}.$$

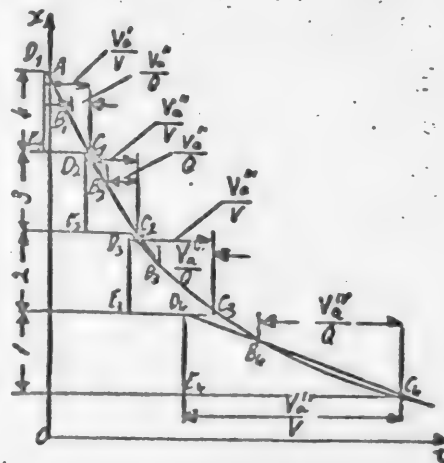


Fig. 9. Calculations for equal falls of concentration, for the optimum regime.

$$Q = f \frac{x_0 - x_k}{m}; \quad m = \text{number of reactors}$$

$$1, 2, 3 \text{ and } 4 - \frac{x_0 - x_k}{m}.$$

b) Calculation for the optimum running conditions. In this case the calculation is carried out in the same way as for the calculation for the optimum running conditions for equal volumes.

The difference is that, in the case in point, the fall in concentration in the system is divided into equal parts, and for each part of the curve a calculation triangle is constructed (Fig. 9).

In a number of cases of this calculation, it is only necessary to calculate the last reactors, which give a specially large increase of the relative CUW and output, so long as the first reactors in any regime work at a sufficiently high relative CUW.

Relative CUW. The relative CUW of the system is the name given to the ratio of the quantity of the reaction mixture, which has reacted in the system under the conditions laid down, to the quantity of substance that would react in a system of reactors having an ideal circulation, the same volume, and the same degree of completion of reaction.

$$\eta_{\text{syst}} = \frac{V}{V_0} = \frac{t_0}{\sum_{i=1}^m t_i} \quad (3)$$

In Fig. 10 is shown the construction of the calculation diagram. In it the triangle $C_1-D_1-E_1$ relates to the first apparatus, into which the initial components enter at the initial concentration X_0 .

The fall of concentration in the first apparatus is determined by the intercept of the ordinate D_1-E_1 . From the first apparatus the partially reacted mixture, at a concentration represented by the point C_1 lying on the $-X$ curve, passes to the second. For the second reactor of the system the triangle $C_2-E_2-D_2$ is constructed in a manner analogous to the first.

In this way as many triangles are constructed as there are reactors in the system.

Graphically, the relative CUW of the system is the ratio of the section $O-C_m$ to the sum of the section C_1-E_1 , i.e.,

$$\eta_{\text{syst.}} = \frac{\text{intercept. } O - C_m}{\sum_{i=1}^m \text{intercept. } (C_i - E_i)}$$

If, as shown in Fig. 10, instead of m reactors (in the given case $m = 2$) one reactor were used, then its volume would be determined by the intercept of the abscissa $C - E_1$ instead of the total volume of the reactors of the system, determined by the intercept of the abscissa $C - F$. Since intercept $(C - E_1) > \text{intercept } (F - C_m)$, consequently, the volume of the single reactor is greater than the sum of the reactors of the system replacing the volume of the single reactor and having an output equal to it. From the graphical construction it is also not difficult to see that the volume of all the reactors of the system decreases with increase

in the number of reactors in the system.

Change of conditions of carrying out reactions in a continuous reactor. A change in the conditions of conducting a reaction in a continuous reactor may be made on the basis of three variants.

Suppose we have a graphical solution, $t-X$, of the process occurring in a continuous reactor, and that we are required to check the possibility of operating it in all three variants. In this case we should have:

Variant 1. $V = \text{const}$; Q decreases to Q_1 (Fig. 11. left).

In this case the task consists in finding, on the curve $t-X$, two points, B_1 and C_1 , which would correspond to the initial and final concentration in the new process, conditioned by the change in the value Q . For this two conditions should be fulfilled:

- 1) The section of the abscissa lying between the ordinates of the points B_1 and C_1 should be expressed on the scale taken by the magnitude $t_c = V_a/Q_1$;
- 2) The straight line drawn through the points C_1 and B_1 to intersection with the line drawn from the point A should give, on the same scale, the value of the intercept of the abscissa lying between the ordinates of the points C_1 and D_1 , equal to the value $t_m = V_a/V$.

For the fulfillment of these conditions the ordinate of the point B_1 gives the value of the new concentration of the mixture X'_D , and the ordinate of the point C_1 gives the value of the new final concentration X'_F .

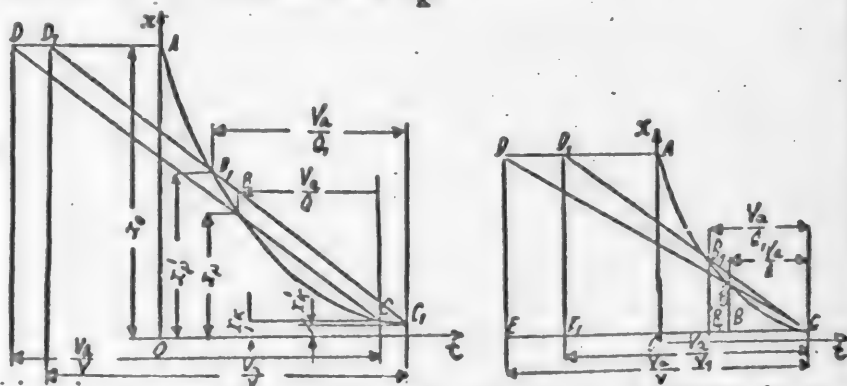
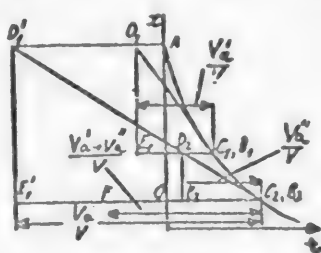


Fig.10. Determination of the relative CUW of the system $Q = \infty$.

Fig. 11. Change of condition of conduct of reactions in a continuous reactor. Left - $V = \text{const}$, $Q_1 < Q$; right $V_1 > V$, $Q_1 > Q$.

Variant 2: The output V increases to the value V_1 ; the output of the mixture decreases from Q to Q_1 (Fig. 11 right).

In this case, from the point of intersection of the ordinate X_k with the axis t , lay off to the left the value V_a/V_1 and draw afterwards a line parallel to the X axis, to intersection with the line drawn from the point A . The point of intersection D_1 coincides with the point C . The intersection of the straight line $C-B_1-D_1$ with the line for the process $t-X$ at the point B_1 gives the value X_p and the intercept of the abscissa $b'-C$, lying between the ordinates of B_1 and C_1 , determines the value Q . We get the maximum output when the point D_1 coincides with the point A and the concentration of the mixture X_p is made equal to X_0 .

Variant 3: $Q = \text{const}$; V increases to V_1 .

The initial concentration X_0 decreases to X_b according to the equation:

$$V(X_0 - X_k) = V_1 (X'_0 - X'_k) \quad (\text{Fig. 12}).$$

On the ordinate axis lay off X_0' and through the point of reference draw a line parallel to the abscissa. The point of intersection of this line with the line C-B-D gives the point D_1 . The intercept of the abscissa laying between the points C and D_1 , gives the value t_m' . This determines the new value V_1 . X_0' is unknown, but V_1 is known then, starting from the point C the value $t_m' = V_a/V_1$ is laid off. From the point of intersection draw a line parallel to the ordinate, to intersection with the line C-B-D. The ordinate of the point of intersection gives the value X_0' .

The minimum concentration of the initial product, for the condition that the process of reaction in the apparatus remains unchanged, is equal to X_p .

In this case the output of the apparatus for unit volume of the initial components becomes equal to the output of the mixer i.e., $V_1 = Q$.

With the help of this construction it is possible to make a check on a process operated in a continuous reactor.

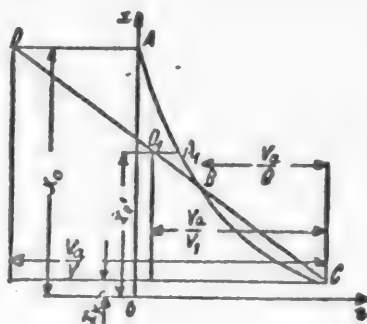


Fig. 12. Change of running conditions of a reaction in a continuous reactor.

$$Q = \text{const}; V_1 = V \frac{X_0 - X_k}{X_0' - X_k}$$

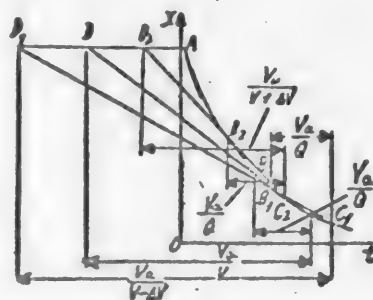


Fig. 13. Graphical check on the process of reaction.

$$Q = \text{const}; (V - \Delta V) < V < (V + \Delta V).$$

Actually if we know that the output of the mixer in the reactor is a completely determinate value then the concentration of the mixture and the final concentration can only be changed as a result of a change either of the volumetric output or of the initial concentration.

Let us consider a process represented by the lines C-B-D and having the output V . With increase of the output to the value $V + \Delta V$ the line C-B-D moves to the position $C_2-B_2-D_2$. The final concentration increases and is represented by the point C_2 i.e. in this case we would have the increase: $X_k'' > X_k$.

When the output decreases to the value $V - \Delta V$ the line C-B-D moves to the position $C_1-B_1-D_1$. The final concentration X_k' decreases and is represented by the point C_1 .

In all cases the period of the reaction $t_c = V_a/Q$ should remain constant.

The control of reaction processes, as is evident, is extremely simple and only requires the previous construction of the curves $t - X$ for the process for the given value Q , and of a series of lines C-B-D with an indication of the outputs to which they relate. The operation of such a control eliminates the need for making extremely complicated and prolonged analyses and proximate analyses. (Fig. 13).

SUMMARY

By the graphical method proposed, continuous reactors or systems of such reactors may be calculated for reactions in the liquid phase when the change of concentration of the initial components of any concentration as a function of time in batch process apparatus is known.

A graphical method permits the determination of: a) The relative CUW of the system and b) the change in the interdependence of the parameters of continuous processes when the conditions under which they operate are changed.

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KINETICS OF CRYSTALLIZATION OF SODIUM BICARBONATE¹

Ya. R. Goldshtein

The physical properties of deposits of sodium bicarbonate precipitated in the course of the carbonation of ammoniacal liquors are of decisive importance for the production of soda. The abnormal course of the crystallization process causes rapid crystallization in towers and a deterioration of the "quality" of the bicarbonate. In washing poor bicarbonate on filters, large losses ensue, the filters give a precipitate with high moisture content which upsets the operation of drying ovens, lowers the concentration of gas and causes a large consumption of heat.

This investigation had the aim of shedding some light on : a) the kinetics of formation of crystallization centers - the conditions of development, existence, and elimination of supersaturation in the carbonation of ammoniacal liquors; b) the role of seed crystals in the kinetics of separation of bicarbonate crystals; c) the dynamics and mechanism of growth and intergrowth of crystals under the conditions existing in carbonation towers, and the limiting size of bicarbonate polycrystals and d) the principles of regulating crystallization under operating conditions.

The formation of very supersaturated solutions in the carbonation of ammoniacal liquors was first established by us in 1926 [1,2,3]. It was found that the crystallization of bicarbonate only begins when the solution contains about 20 "normal divisions" of bicarbonate (1 "normal division", abbreviated to n.d., is equal to 1/20 g-equivalent, i.e., for NaHCO_3 4.2 g/liter). The true solubility of bicarbonate in a carbonated solution does not exceed 3-4 n.d.

The method of studying the phenomenon of supersaturation was not complicated. At the desired point of the carbonation process a sample, volume about 200 ml, was withdrawn and rapidly filtered under vacuum. 10 ml of the filtrate was collected for the analysis, and the remaining liquid was preserved in a closed flask.

According to the reaction $\text{NaCl} + \text{NH}_3 + \text{CO}_2 = \text{NH}_4\text{Cl} + \text{NaHCO}_3$ one equivalent of sodium bicarbonate, precipitated, corresponds to one equivalent of ammonium chloride. Ammonia bound as ammonium chloride was determined by the difference between the "direct titer" of the filtrate, i.e., the titrimetric alkalinity, and the "total titer", i.e., the total content of ammonia, which was determined by formaldehyde titration.

From the primary sample of filtrate, on standing, a precipitate of bicarbonate in the form of fine needles came down. After a definite interval of time a new portion of the clear liquid was collected for analysis. The direct titer in it was lower and the content of bound ammonia was higher than in the first sample. From the increase in the bound ammonia the quantity of bicarbonate precipitated during the time of keeping the sample could be determined.

Let us provisionally represent the supersaturation, determined from the change in composition of the solution over the period of n hours, by P_n . Thus,

¹) Communication II concerning work in the field of the theory and practice of soda production.

for example, analysis of a sample of the clear liquid soon after the collection and a second analysis after two hours, gave us a supersaturation of P_2 and taking a sample once more after three days, we obtained a value P_{72} .

For the observation of the dynamics of the precipitation of bicarbonate, a supersaturated solution was kept for 4-6 hours in a thermostat at the temperature of the experiment. Further observations were made at room temperature. A special control experiment showed that lowering the temperature to that of the room caused no considerable change in the course of the elimination of supersaturation nor did it affect the solubility of the bicarbonate: the error did not exceed one n.d.

For studying the kinetics of the development of supersaturation, carbon dioxide was passed in at a strictly controlled rate. In the majority of experiments we used a glass tube, 30 mm in diameter, height 400 mm, through which a fine tube for introduction of gas was inserted almost to the bottom. The test samples were collected by a pipette with two taps, at the end of which was placed a flannel filter.

The point at which turbidity appeared, i.e., the point at which spontaneous crystallization commenced, was estimated visually as a first step without special precautions. However, in the course of the investigation it became clear that the precipitate of bicarbonate in carbonation comes down in two sharply divided stages: 1) a slow crystallization in which a small number of coarse crystals are produced, creating a turbidity which is scarcely noticeable; and 2) a rapid crystallization resembling an autocatalytic process and leading to the formation of very fine crystals. The first stage may easily be missed by visual observations. Hence the solution was illuminated by a lamp from the side, i.e., a Tyndall cone was created.

EXPERIMENTAL¹

The development and elimination of supersaturation. In Table 1 are given the results of experiments carried out at three standard temperatures: 30, 45 and 60°. In the course of the carbonation of ammoniacal liquors (at a given rate of passage of carbon dioxide) the precipitation of bicarbonate (appearance of turbidity) was noted only after attaining 109 to 117% carbonation C^2 . However, on long standing bicarbonate precipitated even from solutions carbonated only to 84-87%. The point at which the ammoniacal liquors being carbonated became saturated with sodium bicarbonate was found therefore at a value of C equal to 81-82%.

In the experiments of Table 1 the carbonation of the ammoniacal liquors was stopped either at the moment of appearance of turbidity or even before it (after some minutes). The observation of precipitation of sodium bicarbonate (i.e. the systematic analysis of the clear liquor) was carried on for three days. In separate experiments the observation was carried on for ten days; however equilibrium was not

¹) The experimental part of this work relates mainly to 1940-1941 and was carried out with the participation of Chemical Engineer A. S. Rudun.

²) By the % carbonation, here and in the rest of the paper, is meant the ratio of the total quantity of carbon dioxide absorbed, dissolved and entering the precipitate in the form of bicarbonate, to the total content of ammonia in the solution (in n.d. or g. equiv.):

$$\% \text{ carbonation } C = \frac{[2(\text{total-direct titer}) + \text{dissolved } CO_2] \cdot 100}{\text{total titer.}}$$

completely obtained even in this period of time. From the results of the work it is evident that for practical purposes it is sufficient to know P_2 , i.e., to make a second analysis after two hours. This interval was also selected for analysis made during manufacture.

As mixing usually has a strong effect on the elimination of supersaturation [2] then parallel experiments were carried out in which samples were subjected to continuous mechanical stirring for five to six hours. After this the test samples were stored at room temperatures in closed vessels. All data in the table relate to P_{72} , i.e., to the total quantity of bicarbonate precipitated in three days.

In Table 2 are set out data relative to the point at which intense crystallization started at a definite rate of carbonation, based on data in Table 1. The crystallization at the start went extremely quickly; after the first fifteen minutes not less than $2/3$ of the bicarbonate had precipitated in all cases, and 80% came down inside an hour. The further precipitation was much slower.

TABLE 1
Extent of supersaturation and dynamics of its elimination

Temperature (°C)	Duration of carbonation (min)		% Carbonation	Quantity of NaHCO_3 pptd, (in n.d.)											
				Carbonation without stirring						Carbonation with stirring					
	To appearance of turbidity	Total		15 Min.	30 Min.	1 Hrs.	5 Hrs.	24 Hrs.	3 Days	15 Min.	30 Min.	1 Hrs.	5 Hrs.	24 Hrs.	3 Days
30	26	26 (Turb.)	117	14.8	17.6	19.2	22.8	24.4	26.0	-	18.0	-	23.2	23.6	25.2
	-	23	109	5.6	10.0	12.4	16.8	18.8	19.8	5.6	8.8	14.0	17.6	-	19.6
	-	20	102	0.2	1.2	4.0	12.8	13.8	16.8	0.6	3.0	6.0	13.6	13.2	16.8
	-	18	97	0	0	0.4	7.6	9.6	12.8	0	0	2.4	11.2	12.0	13.2
	-	15	87	0	0	0	0	0.8	12.8	0	0	0	0.8	4.4	7.7
45	20	20 (Turb.)	118	15.6	-	17.2	20.5	20.4	23.2	-	-	-	-	-	-
	-	18	110	10.0	12.8	13.6	16.8	17.6	18.8	8.0	13.2	15.0	16.4	16.8	-
	-	15	94	0.4	1.2	2.4	9.6	12.0	14.8	1.6	4.0	7.6	12.8	12.4	14.0
	-	13	86	0	0	0	0.4	3.6	6.4	0	0	0	3.7	4.8	6.0
60	18	18 (Turb.)	109	12.0	13.6	15.0	17.6	18.4	19.6	13.6	15.2	16.0	17.6	18.4	20.4
	-	16	102	5.6	7.2	9.2	12.0	13.2	15.6	10.4	12.0	13.2	14.0	14.8	15.6
	-	14	97	1.0	1.8	3.2	7.6	9.4	9.8	1.4	3.0	-	8.6	9.4	9.8
	-	12	84	0	0	0	0	1.0	2.4	0	0	0	0	1.8	3.0

Quite another picture is presented by experiments in which the carbonation was cut short before the appearance of turbidity. In these cases a definite induction period was always observed. The dependence of the duration of this induction period on the extent of the supersaturation is shown in Fig. 1. When the supersaturation was of the order of 20 n.d. this was only a few minutes, but by the time the supersaturation had fallen to 13 n.d. it had increased to one hour, and at 3 n.d. to 15 hours. Raising the temperature sharply decreased the duration of the induction period. While at 30° the crystallization began after an induction period of 15 minutes when the supersaturation was 17 n.d., at 60° it began after the same period when the supersaturation was only 9 n.d.

This fact is of very great importance for production. The process of carbonation in carbonation towers lasts for 2-4 hours. The zone of the towers in which a temperature of 60° occurs is only about 35% of the height, i.e., the liquid is present in this zone for 40 minutes to 1 hour. In this zone 30 n.d. bicarbonate is usually formed. 10 n.d. bicarbonate is thus formed for $\frac{10.60}{30} = 20$ minutes. The period of

induction for a similar degree of supersaturation is 15 minutes according to Fig. 1. It is known that at 60° it is not possible to develop supersaturation to 10 n.d. By interpolation from the

diagrams given it can be established that at 60° spontaneous crystallization begins at a supersaturation of 8 n.d. In reality, photographic observation of the course of events at different heights of a carbonation tower (Figs. 2 and 3), in which we produced a definite degree of supersaturation, showed that P_2 is 4-5 n.d. Reverting to Table 1, we find that P_2 equal to 5 n.d. corresponds to P_3 of 7-8 n.d. Consequently complete correspondence between the data in Table 1 and plant practice is observed.

The magnitude of the supersaturation at the moment of commencement of intense crystallization has an enormous effect on the rate of development of the crystallization process, as is evident from Fig. 4. The rate of precipitation of the bicarbonate is approximately proportional to the third power of the supersaturation for example, a fact which emerges from Table 3. It is known that the larger the rate of liberation of a substance from solution (crystallization), the smaller the crystals which are thereby obtained. Hence, control of the crystallization process and the magnitude of supersaturation has a great practical significance.

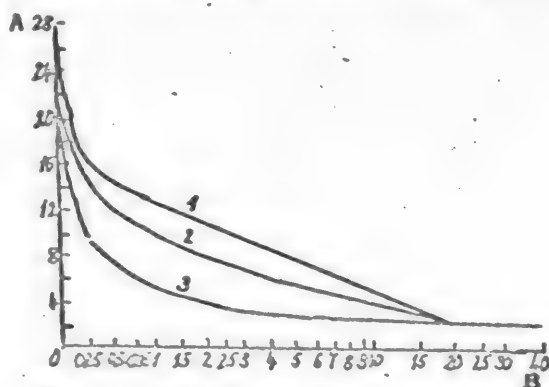


Fig. 1. Effect of degree of supersaturation on the duration of the period of induction. Supersaturation was determined after 5 hours.

A-Degree of supersaturation (in n.d.);
B-induction period (in hours). Temperature (°C): 1-30; 2-45; 3-60.

After each experiment the course of the

TABLE 2

Commencement of rapid crystallization

Temperature (°C)	Time from beginning of carbonation (in min)	Quantity of bicarbonate formed (in n.d.)	Percentage carbonation, %
30	26	26	117
45	20	23	113
60	18	19.6	109

In Table 3 are shown only the initial, more rapid stages of crystallization.

The experiments which were carried out showed that stirring the solutions during the period of elimination of the supersaturation plays an extremely small part, which is unusual in a crystallization process.

Dynamics of change of supersaturation in the successive stages of the process of carbonation. The dynamics of supersaturation are closely connected with the rate of carbonation. They were determined at the same three temperatures of 30, 45 and 60°.

The following experimental procedure was selected. During carbonation the point at which turbidity appeared was noted, but the passage of carbon dioxide was not stopped until definite times; 7, 15, 30 or 60 minutes. The elimination of the supersaturation was

observed, for which purpose the solution was always stirred in a vessel with a mercury seal for 4-6 hours at the experimental temperature. The experimental data are set forth in Table 4 and for separate, longer, experiments in Table 5 (in these figures only the three-hour supersaturation is given).

The special form of the curves for the dynamics of supersaturation can be simply explained. The first portion of the curves up to the peak represents the stage in which supersaturation is accumulating, and the peak itself is the point at which spontaneous crystallization commences. At this point the supersaturation begins to be eliminated at approximately the same rate as that at which it developed (as is evident from the angle formed by both parts of the curve with the perpendicular passing through the peak). The lower scale along the abscissa indicates the quantity of bicarbonate formed at the given point; it is clear that the formation of bicarbonate is practically complete at the end of 90 minutes, when the supersaturation P_3 is 3 n.d. In the following 50 minutes of carbonation the supersaturation is completely eliminated; during this period only 1 n.d. of bicarbonate is formed. The elimination of a residual supersaturation requires, consequently, a considerable time for very little result.

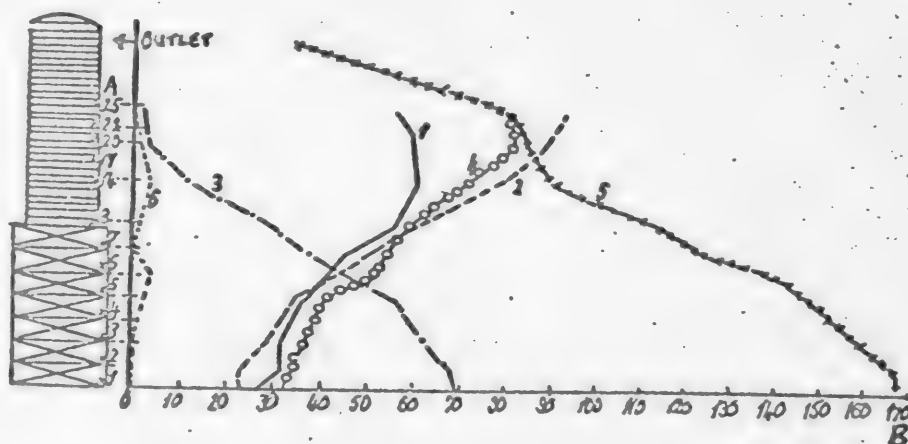


Fig. 2. Photographs of the work of a carbonation tower. Case I. A - Tray No. B - n.d. in degrees; Tower data: 1) temperature; 2) direct titer, (in n.d.); 3) quantity of combined NH_4^+ (in n.d.); 4) quantity of CO_2 in solution (in n.d.); 5) total quantity of absorbed CO_2 (in n.d.); 6) supersaturation.

Tower data (Curve No.)	TRAY NO.										
	1	2	3	5	6	7	8	14	20	22	25
1	26	32	32	37	42	47	57	61	60	60	56
2	22.6	23.6	28.2	35	43.6	51.8	60.4	79	88.8	91.4	93.2
3	69.2	68	63.2	55.6	46.6	36.6	29	11.4	3.2	3.0	2.4
4	33	35	37	42	52	55	60	72	82	82	80
5	167	167	160	148	141	124	114	91	85	84	81
6	0.2	0.4	0	2.6	4.0	0.8	1.6	4.6	1.6	1.0	0.4

The elimination of the supersaturation slows down at 7 n.d. at 30°, at 6 n.d. at 45° and at 4 n.d. at 60° or after the formation of 42, 33, and 30 n.d. of NaHCO₃ respectively. The slow elimination of the supersaturation at the end of the process does not endanger the obtaining of good crystals. On the contrary, it indicates the impossibility of forming new crystallization centers.

The actual magnitude of the supersaturation and its role under plant conditions. Figs. 2 and 3 set forth the results of 2 photographs of the work of a carbonation tower, in which we determined the extent of the supersaturation. From them it is evident how closely the extent of supersaturation is connected with the conditions in, and the results of the work of the tower. For observation of the tower two samples of liquid were selected in parallel, one of which was filtered through a flannel filter and passed immediately through the tap on the pipette (the filtration was made under the pressure of the liquid column). The second was withdrawn in the general course of operation without filtering.

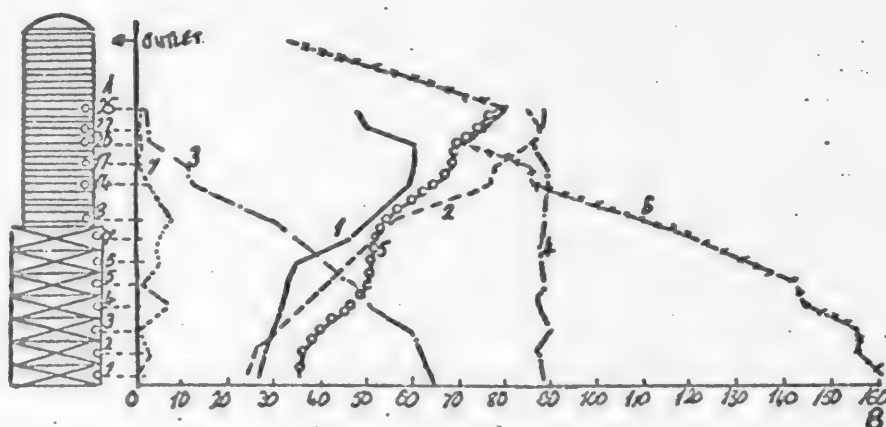


Fig. 3. Photograph of the working of a carbonation tower. Case II. A - Tray No. B - n.d.; 1) temperature; 2) direct titer (in n.d.); 3) bound titer (in n.d.); 4) total titer (in n.d.); 5) quantity of CO₂ in solution (in n.d.); 6) total quantity of absorbed CO₂ (in n.d.); 7) supersaturation.

Tower data (Curve No)	TRAY NO.												
	1	2	3	4	5	6	7	8	14	17	20	22	25
1	27	28	30	32	33	35	47	51	60	61	61	51	49
2	24.8	26.6	31.2	37.4	41.0	47.0	52.6	59.2	77.4	79.6	84.6	86.6	86.6
3	89.4	98.6	91.2	88.6	89.6	88.8	88.4	38.2	90.4	90.6	87.8	89.9	89.4
4	64.6	62.0	66.0	54.2	48.6	41.8	35.8	30	13.0	11.0	3.2	3.2	28
5	35.7	36.7	40.4	47.4	50.8	51.4	52.4	54.4	65.1	69.1	70.1	75.2	79.5
6	161.0	156.7	155.4	145.8	143.9	131.0	120.0	110.4	87.1	87.1	72.5	77.6	81.1
7	0.6	3.6	1.2	7.6	2.8	5.2	5.0	8.6	3.0	1.0	1.4	1.4	1.0

From Fig. 2, which represents the state of affairs in the relatively normal working of a tower, it can be seen that the supersaturation usually does not exceed 4-5 n.d., and such a degree of supersaturation was observed at only two points of the tower. The first point corresponds to the commencement of crystallization of bicarbonate (in the case in point at tray Nos. 14-16).

The second jump in supersaturation appears to be the result of the rapid cooling of the solution at the beginning of the cold zone of the tower (tray 7, Fig. 2.) On cooling the liquid the equilibrium of the reaction is sharply displaced towards the side of an increased yield, very much further from the state of equilibrium, thanks to which the rate of absorption of CO₂ by the liquid increases. Under such a regime bicarbonate of average "quality" is obtained.

TABLE 3

Dependence of the rate of crystallization on the extent of supersaturation. Temperature 30°.

Extent of super-saturation (in n.d.)	Total quantity of NaHCO ₃ precipitated (in n.d.)	Duration of crystallization (in min)	Quantity of NaHCO ₃ precipitated in 1 min (in n.d.)	Relative rate of crystallization
25	18	30	0.6	100
19	13.5	70	0.19	32
15	8	97	0.08	13
10.5	5	180	0.03	5
2.5	2	1380	0.0015	0.25

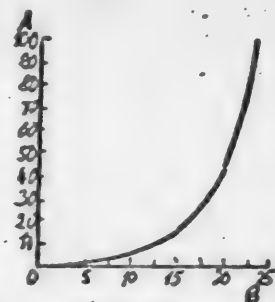


Fig. 4. Effect of degree of supersaturation on the rate of its elimination. Temperature 30°.

A - Rate of elimination of supersaturation (25 n.d. = 100);
B - degree of supersaturation (in n.d. NaHCO₃).

TABLE 4

Dynamics of supersaturation in the process of carbonation.

Dynamics of supersaturation in the process of carbonation.												
Temperature (in deg)	Duration of carbonation (in min)		% carbonation	Bicarbonate precipitated				supersaturation at times of:-			duration of observation (in hrs)	
	to appearance of turbidity	total		at times of.			total	0 min-utes	30 min-utes	3 hrs		
				0 min-utes	30 min-utes	3 hours						
30	29	{	29	116	0	18.0	22.8	25.6	25.6	7.6	2.8	144
			36	125	15.0	25.6	28.4	32.8	17.8	7.2	4.4	139
			44	142	33.5	38.8	41.6	43.6	10.1	4.8	2.0	336
			69	169	53.5	57.6	-	59.2	5.7	1.6	-	89
			89	178	63.0	64.0	-	67.0	4.0	3.0	-	359
45	20	{	20	112	0	17.0	20.0	23.0	23.0	6.0	3.0	50
			27	135	27.0	31.2	33.2	35.6	9.6	5.4	3.4	289
			35	155	37.6	43.2	44.0	47.2	9.6	4.0	3.2	528
			80	167	53.0	54.8	56.0	59.0	7.4	5.6	4.4	139
60	18	{	18	109	0	15.2	17.0	19.0	19.0	3.8	2.0	100
			25	125	18.4	24.0	26.0	30.0	11.6	6.0	4.0	352
			33	140	30.4	33.2	34.8	39.2	7.8	6.0	4.4	311
			48	145	36.6	38.4	39.4	43.8	7.0	5.2	4.2	283

Another picture is shown by Fig. 3. The supersaturation here reaches 8-9 n.d. as a result of fluctuations in the running of the process (concentration of the gas fed in and withdrawal of liquid from the tower). The cooling was too sudden and the temperature fell to 51° by the 8th tray, which intensified the rate of absorption of CO₂ and forced the supersaturation up to 8.6 n.d. The second peak occurs at the 4th tray, and likewise follows a period of rapid absorption of CO₂. In this case the bicarbonate obtained filtered very badly.

Data in the literature about the optimum temperature for absorption of CO₂ in the (ammonia) soda process (45 or 55°) is conflicting. From Fig. 6. it is clear that it is not possible to speak of an "optimum" temperature. The rate of absorption in the initial stages of the process is a maximum at 60° (possibly the maximum rate is at 55°). However the kinetics of absorption begin rapidly, to be determined by the distance from the equilibrium state, which is more favorable at lower temperatures. Hence at 105% the optimum carbonation temperature becomes 45°, and at C = 160% the absorption is most rapid at 30°.

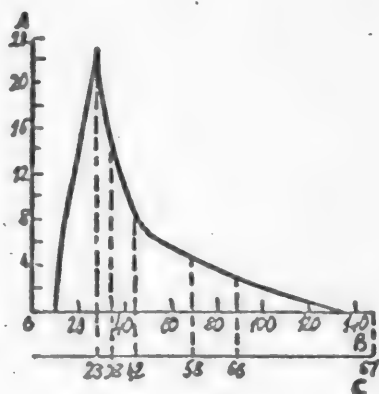


Fig. 5. General dynamics of supersaturation in carbonation at 30°. A - Supersaturation (in n.d. NaHCO₃); B - Time (in min); C - Quantity of NaHCO₃ formed.



Fig. 6. Effect of temperature on the rate of absorption of CO₂. A - Rate of absorption of CO₂ (in n.d./min); B - % carbonation. Temperature (in °C): 1 - 30; 2 - 45; 3 - 60.

Relation between the rate of carbonation and the degree of supersaturation. In Table 5 are set out the results of experiments in which the rate of passage of CO₂ through the solution was changed (0.5, 0.2, and 1.0 liters/min).

At the moment of appearance of turbidity (by the Tyndall cone) a sample of liquid was withdrawn for determination of its supersaturation. The passage of CO₂ was continued for a further 10 minutes, after which it was stopped, and a new sample was withdrawn. It was thus possible to follow both the development and the liquidation of supersaturation.

The data in Table 5 support the expectation of lower supersaturation when the duration of the carbonation is prolonged. The lowering of the supersaturation is particularly significant at higher temperatures, where at a gas rate of 0.2 liter/min it reached only 2 n.d. as opposed to one of 10-15 n.d. at a rate of 1 liter/min.

The dynamics of the change of supersaturation are particularly interesting

in relation to the changes which occur after the commencement of spontaneous crystallization.

Particularly interesting are the dynamics of the changes of supersaturation which follow the commencement of crystallization after 10 minutes carbonation. Contrary to expectation, the supersaturation at low rates of carbonation (0.2 l/min) did not fall, but, on the contrary, increased. This took place at all three temperatures. This would indicate that at low rates of carbonation (meaning also low rates of formation of bicarbonate), the supersaturation should be eliminated at a higher rate than that at which bicarbonate is formed, and especially since crystallization has already commenced. In the meanwhile, at high rates of carbonation, the supersaturation falls.

TABLE 5

Effect of rate of carbonation on the extent of supersaturation.

1. At the point of commencement of crystallization.

Temperature °C.	Duration of carbonation (min)			Quantity of NaHCO ₃ formed (in n.d.)			Supersaturation (in n.d.)		
	Rate of passage of CO ₂ (liter/min)								
	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0
30	90	55	35	8.0	12.6	18.8	8.0	12.6	18.8
45	65	40	26	1.9	8.8	14.5	1.9	8.8	14.5
60	61	31	20	2.3	5.2	9.8	2.3	5.2	9.8

2. 10 minutes from the beginning of carbonation.

Temperature °C.	Quantity of NaHCO ₃ formed (in n.d.)			Quantity of NaHCO ₃ pre- cipitated (in n.d.)			Supersaturation (in n.d.)			Change of supersatur- ation (in n.d.)		
	Rate of passage of CO ₂ (in liter/min)											
	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0
30	11.4	12.3	13.9	6.0	15.4	29.8	13.4	8.5	9.9	+5.4	-4.1	-9.9
45	15.3	15.4	18.6	6.6	16.7	26.5	10.6	7.5	6.6	+8.7	-1.3	-7.9
60	11.9	17.4	20.0	9.4	18.6	25.6	4.8	4.0	4.2	+2.5	-1.2	-5.6

For the elucidation of this phenomenon experiments were carried out with samples withdrawn during the course of carbonation. The carbonation was conducted in a large cylinder with a large volume of liquid, and therefore proceeded more slowly, than in the previous case. The results of one test are set out in Table. 6.

A parallel experiment gave exactly the same result.

The beginning of crystallization was observed after 54 minutes. From Table 6 it can be seen that the crystallization began extremely slowly: after 4 minutes only 1 n.d. of NaHCO₃ had come out. In the course of this time the supersaturation continued to grow steadily. Seven minutes after the beginning of crystallization 2.6 n.d. of NaHCO₃ had come out, and the supersaturation reached 18.4 n.d. At this point where the degree of carbonation was 111.8% (in parallel experiment it was 109.8%) intensive crystallization started, accompanied by a fall in the supersaturation.

As can be seen from Table 6, in the absorption of CO₂ the minimum rate of absorption occurred in the period preceding the maximum supersaturation the

TABLE 6

Kinetics of formation of bicarbonate and elimination of supersaturation in the initial stage of crystallization.
Temperature 45°.

Duration of carbonation.	Composition of filtrate			Composition of filtrate after one day			Quantity of CO ₂ absorbed	Supersaturation (in n.d.)	% carbonation
	Direct titer (in n.d.)	Bound NH ₃ (in n.d.)	CO ₂ (in n.d.)	Direct titer (in n.d.)	Bound NH ₃ (in n.d.)	CO ₂ (in n.d.)			
54	96.0	0.6	95.8	87.2	10.8	77.0	2.5	10.2	100.5
56	96.0	0.8	100.2	81.4	17.0	69.8	1.3	16.2	105.6
53	95.4	1.2	101.4	79.2	18.4	69.6	0.9	17.2	109.2
61	93.8	2.6	100.8	77.2	21.0	67.8	1.1	18.4	111.3
65	87.4	9.4	92.6	74.8	24.0	65.8	-	14.8	115.1

"critical point". As a result of this, a sharp upward jump of the rate of absorption was observed - a "peak". Later on the rate of absorption began to fall, as can be seen from the other data. Consequently, the peak of the rate of absorption follows directly on the critical point and, is undoubtedly connected with it. The critical point is likewise connected with the initiation of intensive crystallization of bicarbonate and the rapid fall in the concentration of carbonate [4,5], and also a jump in the pH [6].

The composition of the solution at this point corresponds, for example, to 110% carbonation, or to 16-20 n.d. of bound ammonia.

Thus, it can be said that at any rate of carbonation intensive crystallization starts at a definite composition of the solution and at a pH of 10. This fact is indisputable evidence that the factors determining the degree of supersaturation, the moment of commencement of rapid crystallization and the peak in the absorption curve, are not a result of the dynamics of the process of absorption, as has been indicated to us by a previous communication [7], on the basis of independent data obtained differently. The observed absorption rate peak may be considerably displaced at large rates of absorption. It begins to break up, however, obligatorily at $C = 110\%$ at 30°.

Extremely interesting results were obtained by the examination of crystals of bicarbonate formed during the period of slow crystallization (when only 1-2 n.d. of bicarbonate is precipitated). Under the microscope these crystals are seen to be excellent spindle shaped crystals of length 100 μ , pointed at the ends and not adhering to one another, (Fig. 7.). At the point of commencement of rapid crystallization the character of the crystals which come down changes sharply, and many fine elongated prismatic crystals with blunt ends, which later on cluster together into curious "tubs", are formed.

It might be thought that the spindle shaped crystals are not composed of pure bicarbonate, but of some compound. However, exactly the same sort of crystal is formed in a tower for the production of "purified bicarbonate" where a solution of ammonia-free sodium carbonate is carbonated. Preliminary analysis of the deposit showed an enhanced content of Na₂CO₃ in it. Carbonates may be present. The data concerning the solubility of salts permit one to speculate about the formation of "trona" Na₂CO₃ · NaHCO₃ · 2H₂O. This question requires careful independent study.

The effect of seed crystal on the rate of elimination of supersaturation.
Introduction of seeds (a considerable quantity of crystals of the substance

expected) should accelerate the elimination of supersaturation, if they are such as to promote crystallization. To elucidate the character of the supersaturation we carried out experiments on the introduction of 30 n.d. of crystalline sodium bicarbonate into the solution immediately after the appearance of turbidity. After the introduction of seeds a mechanical stirrer was started and a sample was rapidly withdrawn. A parallel experiment was carried out without seeds. The experimental data is set out in Table 7.

TABLE 7

Effect of seed crystals on the conditions of elimination of supersaturation. 1. At the moment of appearance of turbidity.

Temp. °C.	Duration of carbonation (in min)			Supersaturation (in n.d.)			Duration of carbonation (in min)			Supersaturation (in n.d.)		
	Rate of passage of CO ₂ (in liter/min)											
	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0
	Without seeds						With seeds					
30	104	63	41	2.0	4.4	9.6	107	62	40	2.0	4.1	9.7
45	71	40	27	0.4	3.0	7.0	72	44	27	0.2	3.0	6.0
60	63	31	20	0.9	2.4	4.2	61	32	18	0.6	1.6	3.6

2. After 10 minutes carbonation, when crystallization had commenced.

Temp. °C.	commenced.											
	Quantity of NaHCO ₃ formed (in n.d.)			NaHCO ₃ precipitated (in n.d.)			Supersaturation (in n.d.)			Change of supersaturation (in n.d.)		
	Rate of passage of CO ₂ (in liter/min)											
	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0	0.2	0.5	1.0
Without seeds												
30	16.6	20.0	18.4	10.0	15.0	18.4	8.6	9.6	9.6	+6.6	+5.2	0.0
45	13.2	19.6	20.0	9.2	16.4	22.4	4.4	6.2	4.6	+4.0	+3.2	-1.8
60	14.6	18.6	22.3	9.7	17.0	24.0	5.8	4.0	2.4	+4.9	+1.8	-1.8
With seeds												
30	16.6	17.8	19.2	12.2	14.4	20.0	6.4	7.6	9.0	+4.4	+3.5	-0.7
45	14.0	19.9	21.8	12.8	20.4	25.8	1.4	2.5	2.4	+1.2	-0.5	-3.6
60	14.7	18.1	22.8	12.6	17.3	24.4	2.9	2.4	2.0	+2.3	+0.8	-1.6

Both the experiments in the first division of the table gave the same result, since the seeds were introduced only at the point of appearance of turbidity. The degree of supersaturation in these experiments was not large, because the carbonation was rather slow. In spite of the presence of a large quantity of crystals, the growth of supersaturation after the start of crystallization in these experiments was even more marked than in Table 5. The supersaturation increased not only at the rate of 0.2 liter/min, but also for 0.5 liter/min and at all three temperatures. The effect of the seed crystals is quite definite; however it is small and does not change the overall picture. At higher temperatures the effect is more marked.

Experiments undertaken with an initial solution of 120% of carbonation gave different results, as shown in Figure 8. In this case a supersaturation of 14 n.d. was attained at the beginning of crystallization (30°), but the introduction into the liquor of a considerably increased number of seeds led to

an immediate decrease in the degree of supersaturation, at a definite duration of carbonation, this decrease in the degree of supersaturation being 8 n.d. at an addition of 60 n.d. of seeds. It can be seen from Figure 8 that the quantity of seeds has a decisive influence on the rate of elimination of the supersaturation. Consequently, at $C = 120\%$, a supersaturation is created which is basically of a crystallizational character.

Nature of the supersaturation. A number of the factors set out above prove that the phenomenon which we have considered to be a normal crystallization supersaturation is of a more complicated character. The crystallization of bicarbonate is evidently inhibited not only by the development of crystallizational supersaturation, but also by the processes which are necessary for the formation of the molecules of NaHCO_3 . These processes and their role in separate stages of carbonation relate not so much to crystallization as to the mechanism of absorption of CO_2 and formation of bicarbonate. From the practical point of view it is a matter of no moment whether we have to deal with a pure crystallizational supersaturation, requisite for the formation of a crystal lattice, or whether we have to deal with a 'supersaturation reaction' in addition. In either case, the effect of the degree of supersaturation and the kinetics of its elimination on the conditions for the formation and growth of crystallization centers and, consequently, on the conditions for obtaining normal sodium bicarbonate is identical. Hence in examining the mechanism of crystallization of bicarbonate and methods for controlling it we can examine the supersaturation as though it had a purely crystallizational character.

We should like, nevertheless, to give some preliminary consideration to the nature of the phenomena examined above.

In the initial stages of the process of absorption of CO_2 , the ammoniacal solution containing a high concentration of free ammonia, and a correspondingly high pH value, forms mainly ammonium carbamate. As the pH of the solution decreases, it follows from the work of Faurcholt [8] and Kirichenko [5] that the equilibrium between carbamate and carbonates in solution is displaced in favor of a higher concentration of ammonium carbonate: at the point of commencement of the precipitation of sodium bicarbonate about 65% of the CO_2 is bound in the form of carbamates and 35% as carbonates. As the process proceeds the carbamates break down and finally only 5-10% dissolved CO_2 remains in this form.



Carbamates are essentially 'parasitic' (side) products, formed due to the ease with which the molecules of NH_3 and CO_2 combine directly without the intervention of water molecules, which are necessary for the hydration of the CO_2 .



The tendency to the formation of carbamate is directly proportional to the quantity of free ammonia (which comprises only part of the dissolved NH_4OH) and of CO_2 in the solution. The quantity of the latter may be considered as constant, because its solubility is limited and only changes slightly during carbonation. The quantity of free ammonia continuously falls as its neutralization proceeds, and correspondingly the tendency to formation of carbamate (according to the law of mass action) falls, i.e. its equilibrium concentration falls.

The quantity $M = \frac{\text{carbamate}}{\text{carbamate} + \text{carbonate}}$ i.e. the fraction of carbamate

CO₂, is a maximum at pH 10, accordingly to Faurcholt.

In the course of neutralization of ammoniacal liquors, with a degree of carbonation equal to 110% (at the critical point), their pH attains the value 10.

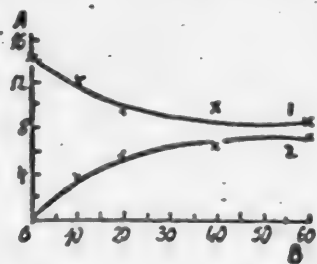


Fig. 8. Effect of seed crystals on the degree of supersaturation.

A) Quantity of NaHCO₃ (in n.d)
B) Quantity of seeds (in n.d)
1) Degree of supersaturation;
2) quantity of NaHCO₃ precipitated. The initial solution was carbonated preliminarily to C = 120%.

The formation of NaHCO₃ proceeds at the expense of the conversion of CO₃²⁻ - ions of carbonate into the HCO₃⁻ ions of bicarbonate by absorption of CO₂:



As the bulk of the CO₂ is initially bound as carbamate, the quantity of CO₃²⁻ ions present in the solution up to the critical point is insufficient for the development in the liquor of a sufficient supersaturation of Na₂CO₃ or NaHCO₃ to ensure crystallization.

In the process of carbonation there is no sharp point at which the breakdown of carbamate is checked. The rate of the breakdown may be increased by accelerating the carbonation, i.e. the neutralization of the ammonia by the CO₂, because as the distance of the system from the equilibrium point increases the rate of movement towards equilibrium increases, i.e. the rate of

decomposition increases. Nevertheless both the hydration of CO₂ and the crystallization require some minimum time, which explains the failure of attempts to achieve carbonation in a few seconds by atomizing the ammoniacal liquor [9] in order greatly to increase its absorbing surface.

The supersaturation which we have studied is therefore of a crystallizational character; its elimination completely follows the usual laws of crystallization. The conditions of the development of this supersaturation, however, are to a considerable degree decided by the conditions for the breakdown of ammonium carbamate which is formed in the first phase of carbonation. This factor has a considerable importance up to the critical point, where a pH of 10 is attained. Its effect on the further course of the carbonation is then small.

SUMMARY

1) In the process of carbonation of ammonia-soda solutions, strongly supersaturated solutions of sodium bicarbonate are formed. The degree of supersaturation may exceed the solubility of sodium bicarbonate 5-7 fold.

2) The intensive, autocatalytic development of crystallization begins only when a sufficient degree of neutralization of the ammonia by CO₂ has been achieved - at 110% carbonation and pH 10 - apart from its dependance on the rate of carbonation. This point is a critical one.

3) When carbonation is stopped before attaining the critical point, a period of induction typical of supersaturated solutions is observed, increasing in length exponentially with decrease in the degree of supersaturation.

4) The rate of crystallization of sodium bicarbonate from supersaturated solution is proportional to the third power of the degree of supersaturation.

5) Raising the temperature and lowering the rate of carbonation decreases the degree of supersaturation. From the experimental data it can be concluded

that at 60° under the actual conditions of operation of carbonation towers, the supersaturation cannot exceed 6-8 n.d., which is confirmed by observations on towers.

6) Stirring has only a small effect on the rate of elimination of supersaturation.

7) Study of the real degree of supersaturation at various heights in a carbonation tower showed that in normal operation the supersaturation does not exceed 4-5 n.d. It is fixed at two points: at the start of crystallization in the hot zone, and at the beginning of sudden cooling of the liquid in the cold zone. With abnormal conditions of operation of a tower the supersaturation may rise to 8-9 n.d., rising at any point where the absorption of CO₂ and consequently, the formation of bicarbonate is increased for any reason.

8) At any rate of carbonation the supersaturation continues to increase after the beginning of crystallization right up to the critical point, where the rate of crystallization sharply accelerates and the supersaturation begins to decrease rapidly. The peak rate of absorption of CO₂ is also in the immediate neighborhood of this point. The break in the course of crystallization and of absorption always occurs in solutions at a definite pH.

9) Slow crystallization may begin earlier than the critical point. In this region extremely well-formed spindle-shaped crystals of bicarbonate are formed, containing an enhanced quantity of sodium carbonate and, possibly, of carbamate. At the point of commencement of rapid crystallization only prismatic crystals with blunt ends, which easily cluster together, are formed.

10) The introduction of crystal seeds before the critical point does not forestall the development of supersaturation. In the further stages of carbonation the presence of seeds does forestall the development of supersaturation above 7-8 n.d.

11) The existence of the critical point and the inefficiency of seed crystals or of stirring demonstrate that the supersaturation is determined not only by crystallizational factors. A preliminary analysis shows that the critical point is connected with the presence in solution of ammonium carbamate or of similar compounds, formed in the initial stages of carbonation. The decomposition of the carbamate, necessary for the formation of carbonates, increases after reaching a pH of 10. This decomposition does not occur at any definite point of the carbonation or crystallization. It may be arbitrarily increased by increasing the rate of carbonation, by increasing the absorbing surface, or by increasing the quantity of CO₂ supplied. Carbamates induce the rapid formation of coarse crystallizational supersaturation at the critical point, which negatively affects the conditions of development of crystals.

The construction and operation of carbonation towers should be aimed at avoiding the formation of such supersaturation by raising the temperature and slowing down the process of carbonation when crystallization starts.

12) The data on the kinetics of absorption of CO₂ obtained during the study of supersaturation showed that the rate of absorption is at a maximum when the temperature is 60°. Beginning at 105% carbonation, the temperature at which the rate of absorption is an optimum is 45° and when 160% carbonation is attained the absorption proceeds rapidly at 30°. It is therefore impossible to speak of any particular temperature as an optimum one for the rate of absorption of CO₂.



Fig. 7. Microphotograph of bicarbonate crystals formed during the period of slow crystallization.

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CHANGE OF ACIDITY OF THE CATHODE REGION

IN THE ELECTRODEPOSITION OF METALS

S. I. Berezina and G. S. Vozdvizhensky.

The importance of the acidity of the electrolyte in relation to the electrodeposition of metals is well known. The change of acidity of the cathode region is of particular importance. However the methods available for measuring this important factor are at present virtually non-existent. In electroplating practice it is usual to be content with a measurement of the acidity of the bath. Attempts to determine the acidity of the cathode region have been made by a number of investigators [1]. They all indicate the presence of a cathode film alkaline by comparison with the bath as a whole. But experiments by one of us [2] have established that the alkalinity of cathode films in the electrodeposition of nickel can reach very high values ($\text{pH} > 8$).

In order to verify and increase the precision of these observations, and with the idea of extending them to other cases of electrolysis, we undertook the working out of an electrolytic method for the determination of the pH in the cathode region during the process of electrolysis, and the adaption of this method to certain processes of great practical importance. For this purpose we selected the metal-hydrogen electrode method, operating simultaneously on the cathodes and the electrolytical cells. The use of metal-hydrogen electrodes for the determination of pH in the space around the cathode in electrolysis is based on the ability of certain metals, such as platinum, nickel, and others, to absorb hydrogen liberated at them during electrolysis and to form as a result a stable hydrogen electrode, i.e., one in which there is a regular change of potential with change of the concentration of hydrogen ions in solution. Being a cathode, the hydrogen electrode is present in the space in which it is desired to measure the pH, and thus can penetrate into spaces which it is practically impossible to reach by other methods.

We studied platinum and nickel as metal hydrogen electrodes.

It is not necessary to give a detailed statement about the basic principles of the use of a platinum-hydrogen electrode, which is well known and widely used. Some details about the nickel-hydrogen electrode will be given.

We selected the nickel-hydrogen electrode firstly because it is known from published sources [3] that in certain circumstances the nickel electrode behaves as a hydrogen electrode, and secondly, because we could determine, with the nickel-hydrogen electrode values of the pH of the cathode region under the same conditions as those in which nickel baths operate.

EXPERIMENTAL

The apparatus for the determination of the pH in the cathode region with the aid of the metal-hydrogen electrode was set up along usual lines. The electrolysis was carried out in a glass vessel, 100 ml capacity. The cathode, around which it was desired to measure the pH of the electrolyte during operation, served at the same time as a metal-hydrogen electrode. As a comparison electrode we used a saturated calomel electrode. To determine the EMF between the calomel electrode and the metal-hydrogen one, a polarizing circuit was switched in and out

by means of an interrupter, enabling us to switch off the polarizing and switch in the measuring circuit instantaneously.

In the first series of experiments, we studied the change in the concentration of hydrogen ions in the cathode region during the electrolysis of solutions of sulfuric acid with platinum electrodes [4]. The cathode was coated with platinum black. Measurement of the EMF was begun 5 minutes after the beginning of electrolysis. The conditions of electrolysis were changed in two directions: by changing the concentration of acid in the solution at constant current density, and by changing the current density in solutions of definite concentration.

The results obtained are set forth in Fig. 1. If the pH values obtained for the cathode region are compared with the av. pH values of the solution, found with a quinhydrone electrode, it emerges that in the electrolysis of 0.1 N H_2SO_4 the pH in the cathode region changes by one unit for change of the current density from 0 to 15 A/dm^2 .

In the electrolysis of 0.01 N solution of sulfuric acid, the curve of current density versus pH is different. At comparatively small c.d.'s, e.g. up to 1 A/dm^2 , the pH of the solution in the cathode region increases slowly with increase in cathode c.d. Later on a very rapid rise of pH with increase of cathode c.d. sets in. When the c.d. changes from 1 to 1.7 A/dm^2 the pH changes from 3 to 10 units.

The rise in the pH-c.d. curve during the electrolysis of 0.001 N H_2SO_4 sets in at considerably lower c.d.'s. Thus, at 0.2 A/dm^2 the pH rises to 10 units, while in the electrolysis of 0.01 N H_2SO_4 such a value is attained only at 1.7 A/dm^2 .

The shape of the curves changes regularly with change of concentration of the acid. The start of the rise in the curve for 0.001 N H_2SO_4 lies somewhere in the region of extremely small c.d.'s.

The second series of experiments was carried out with a smooth platinum cathode.

The conditions were the same as for the first series of experiments. 0.1, 0.01, and 0.001 N H_2SO_4 served as electrolytes. The results obtained are set forth in Fig. 2.

The general character of the pH-c.d. curves are the same as in the first series of experiments, but there is a certain shift, which may be explained by the fact that when set up on smooth platinum, the hydrogen electrode is not completely reversible.

The pH-c.d. curve for the electrolysis of 0.1 N H_2SO_4 shows that for corresponding current densities the pH values are lower than in the first series of experiments. Similarity in the results between the two series was obtained only when approaching a c.d. of 1.5 A/dm^2 .

The rise on the curve for the electrolysis of 0.01 N H_2SO_4 , begins somewhat earlier than in the first experiments, but is not so sharp. A pH of 10 is attained when the c.d. is 2.2 A/dm^2 .

In the electrolysis of 0.001 N sulfuric acid, as in the first series, there was a rapid rise of pH with increase in c.d., only somewhat displaced towards lower c.d.'s. The region where the change of pH with c.d. is gentle lies lower than a pH of about 1.

In parallel with these experiments, others were carried out in which indicators were used. 0.1, 0.01, and 0.001 N H_2SO_4 were subjected to electrolysis. The current

density was changed from 0 to 1.7 A/dm^2 and higher. Phenolphthalein was used as an indicator. The electrodes were of platinum. As a result of these experiments the following information was obtained: in the electrolysis of $0.1 \text{ N H}_2\text{SO}_4$ phenolphthalein does not change color in the cathode region within the limits of the c.d.'s used, which went up to 10 A/dm^2 and higher. The bulk of the electrolyte remained colorless.

Similarly, there was no change in color of the indicator in the electrolysis of $0.01 \text{ N H}_2\text{SO}_4$ at lower current densities, but at c.d.'s of $1.5\text{--}1.7 \text{ A/dm}^2$ a very thin pink layer appeared around the cathode.

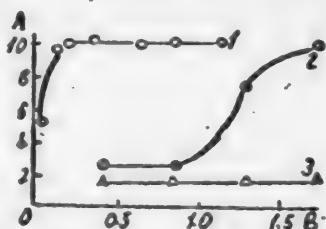


Fig. 1. Effect of change on the pH of the cathode solution in H_2SO_4 of different concentrations with cathodes coated with platinum black.

A - Concentration of hydrogen ions
B - Current density (A/dm^2). 1 - $0.001 \text{ N H}_2\text{SO}_4$; 2 - $0.01 \text{ N H}_2\text{SO}_4$; 3 - $0.1 \text{ N H}_2\text{SO}_4$.

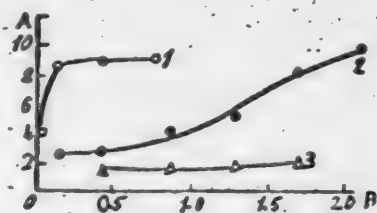


Fig. 2. Effect of change of c.d. on the pH in difference concentrations of H_2SO_4 at a smooth platinum cathode.

A - Concentration of hydrogen ions
B - Current density (A/dm^2).
1 - $0.001 \text{ N H}_2\text{SO}_4$; 2 - $0.01 \text{ N H}_2\text{SO}_4$; 3 - $0.1 \text{ N H}_2\text{SO}_4$.

The change in color of phenolphthalein in the cathode region during the electrolysis of $0.001 \text{ N H}_2\text{SO}_4$ occurred at a c.d. as low as $0.1\text{--}0.2 \text{ A/dm}^2$. Here the volume of the colored space was larger. The coloration of the indicator also appeared much sooner after switching on the current (1-2 secs), and disappeared considerably more slowly after switching off than in the electrolysis of $0.01 \text{ N H}_2\text{SO}_4$.

The results of experiments using indicators are in full accord with the results obtained when using the hydrogen electrode.

It is known that the region of transition of phenolphthalein from the colorless to the colored form lies at pH's of $8.3\text{--}10.5$. The coloration of the phenolphthalein in the cathode region occurred in the electrolysis of the 0.01 N acid, commencing at a c.d. of $1.5\text{--}1.7 \text{ A/dm}^2$, corresponds to the character of the curves shown in Fig. 2. The appearance of color in the electrolysis of 0.001 N acid occurs at the same current density as that at which the curve for the corresponding solution (Fig. 2) bends round, lying at $8\text{--}9 \text{ pH}$.

These results appear to confirm the results obtained with the platinum-hydrogen electrode.

In the following series of experiments the change of the concentration of hydrogen ions in the process of the electrodeposition of nickel was studied. Initially we will deal with experiments using cathodes of smooth platinum.

The electrolytes were nickel sulfate solutions of different concentrations in $0.001 \text{ N H}_2\text{SO}_4$. The concentration of nickel sulfate in the electrolyte was varied from 0.1 to $1.7\text{--}1.8 \text{ N}$, i.e., it approached a value generally used in nickel-plating baths. The results are presented in Fig. 3.

The pH was calculated on the assumption that the platinum electrode behaves as a hydrogen electrode under these conditions, and that to a certain degree of approximation it reflects changes in the hydrogen ion concentration of the cathode region, and on the assumption that the main portion of the cathode potential is determined by the rate of discharge of hydrogen ions and not of nickel ions.

The experiments showed that in the electrolysis of the solutions mentioned, at a c.d. of 0.2 A/dm^2 , and when the nickel concentration was low ($0.1\text{--}0.9 \text{ N}$), there was a considerable elevation of the pH - up to 11-13 units. Under these conditions hydrogen was discharged almost exclusively on the cathode, and a strong alkalization of the cathode region was produced, conditioned by the precipitation, in the immediate neighbourhood of the electrode, of basic salts of nickel in large quantity. Beginning at $0.1\text{--}0.9 \text{ N}$ nickel sulfate, metallic nickel, usually of a black or greyish color, was deposited on the cathode. The pH in these cases stayed fairly constant at a lower value (≈ 8.5).

At a cathode c.d. of 0.5 A/dm^2 the range of nickel sulfate concentration, characterized by the strong alkalization and by a large amount of basic nickel salt precipitated from the solution, was considerably displaced. It was covered by a change of nickel sulfate concentration in the solutions investigated from 0.1 to $1.1 - 1.2 \text{ N}$.

At a nickel sulfate concentration of $1.3 - 1.5 \text{ N}$ a more marked deposition of metallic nickel on the electrode occurred.

The pH of the electrolyte at which metallic nickel discharged at the cathode always remained about 9.5.

In the electrolysis of the solutions at a cathode c.d. of 0.8 A/dm^2 , no change of pH with change of nickel sulfate concentration, within the limits of our observations, was found. The pH always remained high (≈ 12). Basic salts were observed in the cathode region under these conditions.

At lower nickel sulfate concentrations higher pH's in the cathode region were observed. This was even visually obvious in the deposits of basic nickel sulfate precipitated.

The cathode current density similarly had a notable effect on the change of the acidity of the electrolyte in the cathode region. At concentrations of nickel sulfate at which the pH kept more constant, a quite definite correlation exists between the change of pH and the cathodic c.d. The higher the D_K , the larger the pH which is attained by the electrolyte bathing the cathode.

All experiments carried out with nickel cathodes can be divided into two groups. In the first group the objective was to follow the changes of pH, determined by the nickel electrodes, as they were affected by changes in the cathode c.d. and by changes in the concentration of nickel sulfate in the electrolyte. The experiments in the second group were designed to establish the change of pH of the electrolyte in electrolysis with change of concentration of nickel sulfate and of sulfuric acid.

The experiments of the first group were analogous to those with platinum cathodes described above. The difference in these experiments consisted in the fact that nickel-plated plates, prepared from pure nickel were used as cathodes. Before each determination, the nickel cathodes were treated as follows: they were first carefully degreased with concentrated Na_3PO_4 , after which they were washed with water and plated in the usual nickel bath for 10 minutes. After this preliminary preparation they were washed with water, rinsed with the

electrolyte to be used in the experiment, and then inserted into the circuit as a cathode. After 4 and 5 minutes of electrolysis, in the course of which equilibrium was established, the potential of the cathode was measured. A platinum plate was used as anode.

The electrolyte as in previous experiments with a platinum cathode, was 0.001 N H_2SO_4 containing different amounts of nickel sulfate. The concentration of NiSO_4 changed from 0.1 to 1.9 N. The cathode current density changed from 0.2 to 1.6 A/dm^2 .

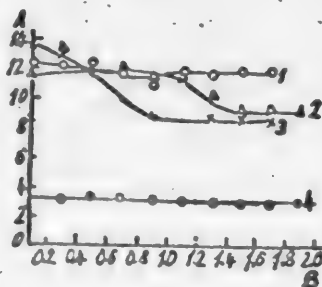


Fig. 3. Effect of concentration of NiSO_4 at different current densities on the change of the pH at a platinum cathode. A - Concentration of hydrogen ions. B - Concentration of NiSO_4 . Current density (in A/dm^2): 1 - 0.8; 2 - 0.5; 3 - 0.2. pH values found: 1 - 2 and 3 - on platinum hydrogen electrode; 4 - on quinhydrone electrode.

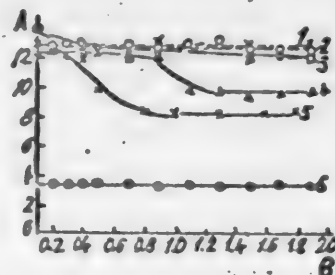


Fig. 4. Effect of concentration of nickel sulfate (N) at different current densities on the pH at a nickel cathode. A - Hydrogen ion concentration; B - NiSO_4 concentration (N). Current densities (in A/dm^2): 1 - 1.6; 2 - 1.2; 3 - 0.8; 4 - 0.5; 5 - 0.2. pH values obtained: 1, 2, 3, 4 and 5 - at a nickel hydrogen electrode; 6 - at a quinhydrone electrode.

The data obtained with nickel electrodes are shown in Fig. 4. The values of the pH, calculated from the potential of the cathode, changed during electrolysis. Calculations were made via the formula for the hydrogen electrode in accordance with the literature references mentioned above, according to which the nickel electrode, under certain conditions, behaves as a hydrogen electrode.

The data obtained show that in general the pH of the cathode region depends on the density of the polarizing current and the concentration of nickel sulfate in the solution, and that the nature of the changes involved is similar to that already seen for the smooth platinum cathode. Thus, as in the first case, where the concentration of nickel was such that a constant cathode potential was reached, the pH increased regularly with increase in current density. With increase in the c.d. from 0.2 to 0.8 A/dm^2 the pH increased sharply, from 8.2 to 12.1 units. With further increase in the cathode c.d. the pH increased more slowly. Thus, with increase of D_k from 0.8 to 1.6 A/dm^2 the pH increased from 12.1 to 12.7.

It should also be noted that there is a certain divergence between the data obtained at a nickel cathode, and that obtained at a platinum cathode.

Thus, at a current density of 0.2 A/dm^2 , with a nickel cathode the pH approaches a constant value at a lower concentration of nickel sulfate than at a platinum cathode ($0.75\text{--}0.80 \text{ N}$ compared with 0.95 N), but the pH is $0.3\text{--}0.4$ units lower than that observed on the platinum cathode.

At a cathode current density of 0.5 A/dm^2 on a nickel cathode the pH approaches a constant value for a nickel sulfate concentration of about 1.2 N as compared with 1.5 N on a platinum cathode. The pH obtained on a nickel cathode is about 0.2 units higher than that on a platinum one. The pH's obtained at 0.8 A/dm^2 are nearer. Thus within the limits of nickel sulfate concentration of 1.5 to 1.8 N they differ only by $0.1\text{--}0.2$ units.

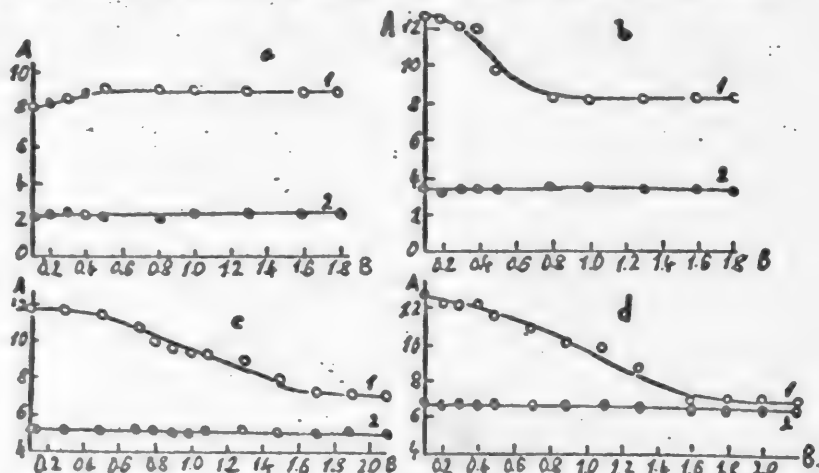


Fig. 5. Effect of the initial concentration of H_2SO_4 and of NiSO_4 on the pH of the electrolyte around the cathode.

A - pH; B - NiSO_4 concentration (N): 1 - at a nickel-hydrogen electrode, 2 - at a quinhydrone electrode. Concentration of H_2SO_4 (N): a - 0.01 , b - 0.001 , c - 0.00001 , d - 0.0 (pure water).

The experiments of the second group with nickel cathodes were designed to follow the changes of the pH in the cathode region as a function of the initial concentration of the nickel sulfate and of the sulfuric acid in the electrolyte. The concentration of nickel sulfate was changed from 0.1 to 2.2 N , and the sulfuric acid from 0 to 0.01 N .

All the experiments were carried out with platinum anodes and nickel cathodes, prepared in advance as in the previous experiments. The cathode c.d. employed was 0.2 A/dm^2 . For each freshly prepared solution the pH was determined with a quinhydrone electrode.

The results of the experiments are presented in Fig. 5 (a - d).

The results obtained show that in the electrolysis of all the compositions that we investigated, there is a region in which the pH is constant, beginning at a certain quite definite value of the nickel concentration. It is characteristic that the higher the pH of the initial solution, the lower the difference between the latter and the pH found in the cathode space with the aid of the nickel electrode at the beginning of the electrolysis.

Thus, in the electrolysis of 0.01 N H_2SO_4 containing nickel sulfate this difference reached 6.5 units, and in the electrolysis of 0.001 and 0.00001 N solutions with the same addition of nickel sulfate the differences were, respectively, 4.9 and 2.2 pH units. If the initial electrolytic solution is an aqueous solution of nickel sulfate, containing no sulfuric acid, then this difference is only 0.5 units.

DISCUSSION OF RESULTS, AND CONCLUSIONS.

The method we used for determining the H ion concentration in the cathode region in the electrodeposition of nickel and the electrolysis of sulfuric acid has completely justified itself.

Metal-hydrogen electrodes, as we have seen, can reflect the pH of liquid around the cathode under a wide range of conditions.

The metal-hydrogen electrode method can, apparently, be reckoned as unique in its ability to penetrate into regions in the immediate neighbourhood of the cathode. The pH's found by this method are in complete agreement with the results of observations made with indicators.

The pH of the cathode space shows a regular dependance on the current density, on the general H ion concentration, and on the concentration of metal ions in the solution. For nickel this dependance agreed well with the current efficiency for the metal as a function of the hydrogen ion concentration.

The experimental results obtained make it possible to claim that the task of determining the pH of the liquid around the cathode during the electrolysis of nickel is in the main solved.

From analysis of the experimental material relative to the change of pH of the cathode space in the electrolysis of nickel sulfate and sulfuric acid at different concentrations of sulfuric acid, it emerges that under these conditions a considerable alkalization of the cathode space occurs.

Thus the results of measurement of the pH of the cathode region with a platinum hydrogen electrode show that in certain cases this alkalization may reach a pH of 9-10. The pH of this space is mainly dependent upon the H ion concentration in the electrolyte and the current density used. Such a large alkalization is due to the non-equivalence of the rates of two processes: the rate of discharge of hydrogen ions, and the rate at which the concentration of hydroxyl ions is balanced out by diffusion.

The electrolysis of solutions of sulfuric acid is the simplest case; here only one ionic species is discharged at the cathode - H ions. In more complex cases, where other ions are discharged simultaneously with H ions, the process is considerably more complicated. As an example, may be taken the electrolysis of nickel in the presence of sulfuric acid, which we investigated, and where there is a simultaneous discharge of nickel and hydrogen ions.

In cases where the cations yield compounds of low solubility with hydroxyl ions, they precipitate in the form of insoluble hydroxides or basic salts. In other cases the cations may yield soluble compounds with hydroxyl ions. The concentration of hydrogen ions in these cases may be determined by the dissociation constants of these compounds. When there is simultaneous discharge of metal and hydrogen ions, the change of the pH in the cathode layer depends on the current efficiency for the metal and for hydrogen. The larger the current efficiency for hydrogen, the higher the pH may go. The current efficiency for metal and hydrogen in its turn depends on the current density and the pH of the

solution undergoing electrolysis. Therefore, in order to elucidate the real state of affairs in the cathode region all these factors must be examined for their mutual influence on one another.

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ELECTRODE POTENTIALS IN THE ELECTROLYSIS OF DIFFERENT SALTS AT

A MERCURY ELECTRODE ¹

P. P. Tsyb and M. T. Kozlovsky

S. M. Kirov State University, Kazakh

In the previous communication it was noted that our investigation was directed to the study of the effect of different factors both on the cathode process in the electrolytic deposition of metals, and on the anodic decomposition of amalgams. The work reported here was aimed at elucidating the effect of certain factors on the potential of the cathode and anode in the electrolysis of salts of tin and cadmium. ✓

The potential of amalgams containing different quantities of tin and cadmium have been the subject of detailed study [2,3]. However these investigations were directed to the elucidation of the physical properties of amalgams, and not for utilizing the results obtained in electrolysis. The discharge potential of metals on a mercury electrode has been studied polarographically [4-5]; these results may to a certain extent be used for electrolysis with the normal mercury electrode. But account must be taken of the fact that in electrolysis with the dropping mercury electrode extremely dilute amalgams are obtained and the cathode is continuously renewed, while in electrolysis with the ordinary mercury electrode the concentration of metal increases during electrolysis, which increase should cause a change of potential.

The experiments on the electrolysis of tin and of cadmium salts were carried out along the same lines as those reported in the previous communication [1]. The conditions and methods of carrying out the experiments were the same as in the electrolysis of copper reported there [1].

EXPERIMENTAL

Electrolysis of tin salts. The solution of tin sulfate used in these experiments was prepared by treatment of stannous chloride with concentrated sulfuric acid in the presence of metallic tin, with subsequent removal of excess HCl by evaporating down the mixture, the residue being dissolved in $N H_2SO_4$.

Chemical analysis did not reveal any impurity in the stannous sulfate, but spectrographic analysis did reveal traces of lead, zinc, silver, copper, iron, manganese and calcium.

The tin was determined gravimetrically as stannic oxide in the solutions prepared. In the electrolytic deposition of tin on a mercury cathode, attempts were made to separate it completely from a solution containing sodium sulfide and gold chloride [6].

Initially experiments were carried out on the deposition of tin on a mercury

¹) Communication II in a series on this theme.

cathode and on electrolytic decomposition of the amalgams obtained. For this purpose 200 ml of a solution of known tin content, 1 N in sulfuric acid, were placed in an electrolyzer, and precipitation of tin on a mercury electrode was carried on with simultaneous measurement of the cathode potential. After complete separation of the tin the polarity was reversed so that the amalgam became the anode, and the platinum gauze the cathode, and the amalgam obtained was decomposed electrolytically with simultaneous measurement of the anode potential. The electrolysis was carried on until no black turbidity was present in the electrolyte as a result of the transfer of ions of mercury into the solution, which were then reduced to the metallic state by interaction with the tin ions, this point being indicated by a sudden rise in the anode potential. After this the electrolysis was stopped, the mercury separated from the electrolyte, and the tin in the solution determined quantitatively.

The experimental data on the electrolytic deposition of tin are presented in Table 1, and those on the electrolytic decomposition of the amalgam in Table 2.

From the data of Table 1 it follows that, under the conditions of these experiments, the current efficiency where the tin was completely separated from the solution was 25-50%, which is explained by the simultaneous discharge of hydrogen ions especially towards the end of the electrolysis when the concentration of tin in the electrolyte became very small, and also when current was consumed in reducing tetravalent tin, obtained by the anodic oxidation of divalent tin, and also by oxidation with atmospheric oxygen.

From the data in Table 2 it emerges that the current efficiency in the electrolytic decomposition of amalgams, with formation of divalent tin ions in solution is 107%. The deviation from 100% may be explained by the oxidation of divalent tin to tetravalent by atmospheric oxygen, and the reaction of the latter with the tin in the amalgam, causing a transfer of tin into solution: $\text{Sn} + \text{Sn}^{4+} \rightarrow 2\text{Sn}^{2+}$.

Quantitative determination of the tin going into the solution from the amalgam, showed that the tin in the amalgam can be practically completely extracted from the amalgam by this method.

In the following series of experiments, the aim was to find out the dependence of the potential of the cathode and anode on the concentration of tin in the amalgam. For this purpose amalgams containing 0.01, 0.1, 1, 2, 4, 8 g-atoms of tin per liter of mercury were made by the electrolysis of solutions of stannous sulfate having known tin concentrations, and measurements of cathode potential and - after changing the polarity - of anode potential were made. All the measurements were carried out on 200 ml of 0.1 molar stannous sulfate, containing 1 g-equiv of sulfuric acid. The experimental data are presented in Table 3.

From the experimental data presented in Table 3 it is evident that with increase in the concentration of tin in the amalgam the cathode potential displaces toward more negative values. However this was observed only up to a concentration e.g. of 1 g-atom Sn/liter of mercury in the amalgam and with further increase in the concentration of tin in the amalgam the potential of the cathode did not change.

It should be mentioned that Pushin [2] measured the difference of potential of amalgams, with different concentrations of tin, relative to metallic tin, in 1 N solution of stannous chloride, obtaining the following values:

Atoms % Sn	:	0.0	1.32	30	46-66.6	75.3	83.4	93.9
Difference of potential (V):		0.5000	0.0015	0.0007	0.0010	0.0012	0.0010	0

Other authors [7-8] measured the difference of potential of amalgams at different contents of tin relative to an amalgam containing 16 g-atoms %, and likewise observed that with increase in the concentration of tin in the amalgam the difference in potential decreases only up to a concentration of 0.96-1.2%, and thereafter remains constant to 99% atom %.

Similar phenomena emerges from our experimental data, though our investigations were carried out under other conditions. It may be suggested that the phenomenon is due to the formation of two phases. For concentrations of tin from 0.01 to 1 g-atom Sn/liter of mercury, the potential difference at a temperature of 18-23° is 0.05 V, i.e. corresponds for example to the theoretical value calculated from the formula of Turin for the amalgam concentration cell:

$$E_2 = E_1 + \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

When the concentration of tin in the amalgam is increased further a saturated solution, i.e. a two-phase system, is obtained and crystals of tin separate. From here on the concentration of tin in the amalgam remains constant, hence the potential of the cathode from then on does not depend on this concentration.

From the experimental data presented in Table 3, it can be seen that when anode polarization occurs there is the same dependence of the anode potential on the concentration of tin in the amalgam, as in the cathodic process. However the difference in potential between the amalgam with different concentrations of tin is less than in the cathodic polarization of the same amalgam.

The effect of temperature on the cathode and anode potentials can be seen from the experimental data in Table 3.

With elevation of the temperature, concentration polarization and hydrogen overvoltage decrease, and as a result the cathode potential should become more positive, which is actually observed. However as the temperature rises the potential only becomes slightly more positive, which is explained by the fact that at higher temperature the tin salts in the solution hydrolyze.

With anodic polarization, increase of the temperature decreases the concentration polarization, which should cause a displacement of the anode potential to more negative values, and this is indeed observed in the experimental data for low concentration amalgams. At higher concentrations of tin in the amalgam its concentration in the surface of the mercury electrode also increases, and as a result diffusion of tin has a smaller effect than in more dilute amalgams, so that the anode potential practically does not depend upon temperature.

From the experimental data of Table 3 it is evident that with increase of the current density the potential of the cathode displaces towards more electro-negative values, while the potential of the anode becomes more electropositive: these results, if plotted, would be reflected in a linear course of the corresponding potential curves.

The next experiments were made to elucidate the effect of concentration of tin in the electrolyte on the anode and cathode potential. For this purpose amalgams were prepared containing 1 g-atom of tin per liter of mercury, and measurements of the potential of the cathode and afterwards of the anode were

TABLE 1

Experimental data on the deposition of tin on a mercury cathode*

Experimental data on the deposition of tin				Change of cathode potential (V) with time (Min)												Current efficiency (%)
Initial concentration of tin in the electrolyte (in g)	Current density (A/cm ²)	Potential (V)	Temp. (°C)	9	5	10	15	20	25	30	35	40	45	50	65	
1.1870	0.11	6-6.3	20	0.82	1.26	1.44	1.47	1.50	1.54	1.54	1.54	1.54	-	-	-	25.7
1.1870	0.11	5.7-5.8	50	0.72	1.22	1.48	1.50	1.50	1.54	1.54	1.54	1.54	-	-	-	25.7
1.1870	0.055	4-4.3	20	0.60	0.92	1.12	1.22	1.16	1.28	1.30	1.34	1.34	1.34	1.34	1.34	36.7
1.1870	0.055	4.1-4.8	50	0.44	0.80	1.08	1.22	1.26	1.26	1.26	1.28	1.28	1.28	1.28	1.28	36.7
2.3740	0.11	6.5-6.7	20	0.78	0.98	1.28	1.42	1.52	1.54	1.56	1.58	1.58	1.58	1.58	-	36.7
2.3740	0.11	5.5-5.3	50	0.66	0.88	1.22	1.42	1.48	1.50	1.50	1.56	1.56	1.58	-	-	36.7
2.3740	0.055	4.3-5.2	20	0.44	0.50	0.66	0.92	1.10	1.18	1.20	1.24	1.28	1.32	1.34	1.34	51
2.3740	0.055	4.2-4.7	50	0.43	0.48	0.74	0.86	1.12	1.24	1.29	1.31	1.30	1.30	1.32	1.32	51

*The potentials given in Table 1 and in all other tables are relative to the normal hydrogen electrode: in Table 1 they are negative, and in Table 2 positive, except where indicated by a (-) sign.

TABLE 2

Experimental data on the decomposition of tin amalgams

Initial concentration of tin in the amalgam (in g)	Current density (A/cm ²)	Potential (V)	Temp. (°C)	Change of anode potential (in V) with time (Mins.)										Tin found after decomposition of amalgam (in g)	Deviation (in %)	Current efficiency (%)
				0	3	5	6	7	8	10	12					
1.1870	0.11	3-4	20	0.14	0.16	0.18	0.20	1.04	-	-	-	1.1792	0.73	107		
1.1870	0.11	2.8-4	50	0.16	0.18	0.18	0.22	1.0	-	-	-	1.1784	0.72	107		
1.1870	0.055	1.5-3	20	-0.14	-0.13	-0.12	-0.12	-0.12	-0.12	-0.12	0.78	1.1754	0.96	107		
1.1870	0.055	1.6-3	50	-0.07	-0.06	-0.04	-0.04	-0.03	-0.02	-0.01	0.72	-	-	107		
2.3740	0.11	3.2-4.5	20	0.14	0.17	0.19	0.19	0.19	0.20	0.22	1.04	-	-	107		
2.3740	0.11	2.5-3.6	50	0.16	0.18	0.19	0.19	0.19	0.20	0.20	1.02	-	-	107		

carried out. The measurements were made with 200 ml of solution, containing 1 g-equiv. of sulfuric acid and 0.01, 0.05, 0.1 and 0.5 g-ion of tin per 1 liter of electrolyte.

The experimental data are set out in Fig. 1.

It is evident from these results that with increase of the tin concentration in the electrolyte, both the potential of the anode and of the cathode are displaced towards more electropositive values, as they should be from Nernst's formula. Furthermore, from the course of the potential curves it is evident that at small concentrations of tin in the electrolyte the polarization curves for the cathode are strongly displaced towards the more electro negative regions, this occurring particularly at higher current densities, which is connected with the concentration polarization. As is evident from the course of the potential curves, the concentration polarization has a smaller effect on the potential in the anodic process, than in the cathodic. From this it follows that in the electrolytic decomposition of amalgams the concentration of tin in the electrolyte has only a small effect on the anode potential. This is due to the fact that while the cathode process is limited by the diffusion of ions to the cathode, in the anodic process the main part is played by the rate of diffusion of the atoms of tin to the surface layer of the amalgam.

The following experiments threw light on the influence of electrolyte acidity on the cathode and anode potential. The potential curves were taken for amalgams containing 1 g-atom of tin per liter of mercury. 200 ml of solution served as electrolyte, containing 0.1 g-ion of tin per liter, with acidities of 0.1, 1, 2, and 4, N (sulfuric acid). The experimental data are shown in Fig. 2.

It follows from these data that with increase in the acidity of the electrolyte, the potential both of the anode and of the cathode are displaced towards more electronegative values. This is connected with the diminution of the activity coefficient of the ions, as a result of the increase of the ionic strength of the electrolyte.

Electrolysis of cadmium salts. A solution of cadmium sulfate was prepared from salt which was shown spectrographically to contain only very small quantities of tin, zinc, copper, iron, manganese and calcium, below the limit of chemical detection.

The cadmium content of solution was determined gravimetrically as the sulfate [9]. The attempts at complete separation of cadmium from an electrolyte were made with the aid of sodium sulfide [6]. The conditions and methods of carrying out the experiments with cadmium were the same as in the experiments with tin.

The results of the precipitation of cadmium on a mercury cathode and the electrolytic decomposition of the resulting amalgam are set out in Tables 4 and 5.

From the results in Table 4 it will be seen that when cadmium was quantitatively deposited under the conditions given, the current efficiency was 27-81% on account of the simultaneous discharge of hydrogen. Raising the temperature increases the current efficiency, since it diminishes the concentration polarization. Increasing the concentration of cadmium also increases the current efficiency, as under these conditions a large part of the energy is consumed in the discharge of the cadmium ions and a lesser amount in discharging hydrogen ions.

In the electrolytic decomposition of amalgam (Table 5) as the cadmium concentration in the amalgam is decreased the anode potential gradually becomes

TABLE 3

Dependence of the cathode and anode potential on the concentration of tin in the amalgam ¹

Concentration of tin in the electrolyte (in g-atoms/liter)	Temperature (in deg)										
	18-23							48-53			
	Current density										
	0.0022	0.011	0.022	0.044	0.055	0.07	0.09	0.11	0.0022	0.011	0.022
Cathode											
0.01	0.23	0.26	0.30	0.39	0.44	0.50	0.60	0.72	0.24	0.27	0.32
0.1	0.26	0.30	0.34	0.42	0.47	0.53	0.62	0.71	0.26	0.29	0.34
1	0.28	0.30	0.34	0.44	0.48	0.54	0.64	0.76	0.27	0.30	0.34
2	0.27	0.30	0.34	0.42	0.47	0.53	0.63	0.76	0.28	0.30	0.35
4	0.28	0.30	0.34	0.43	0.48	0.54	0.64	0.77	0.28	0.30	0.35
8	0.27	0.30	0.34	0.42	0.48	0.54	0.64	0.75	0.27	0.30	0.34
Anode											
0.01	0.25	0.22	0.18	0.10	0.06	0.01	-	-	0.26	0.24	0.19
0.1	0.28	0.24	0.20	0.13	0.08	0.04	+0.04	+0.12	0.27	0.23	0.20
1	0.28	0.26	0.21	0.13	0.10	0.04	+0.04	+0.12	0.28	0.25	0.20
2	0.28	0.26	0.21	0.13	0.10	0.05	+0.03	+0.12	0.28	0.25	0.21
4	0.28	0.26	0.20	0.12	0.08	0.04	+0.05	+0.15	0.28	0.25	0.20
8	0.28	0.25	0.20	0.12	0.08	0.04	+0.05	+0.16	0.28	0.25	0.20

more electropositive, as in the similar experiments with tin, and at the end of the electrolysis a white turbidity appears in the electrolyte, as a result of the oxidation of mercury and the formation of the low solubility of mercurous sulfate. At this point the potential rises to values necessary for the oxidation of mercury under the conditions given. The current efficiency in these experiments was higher than 100%, apparently due to the direct interaction of cadmium with sulfuric acid (local cell formation).

The next series of experiments were devoted to the effect of the concentration of cadmium in the amalgam on the anode and cathode potentials at different temperatures and different current densities. The experimental data are set out in Table 6.

From these results it follows that with increase in the concentration of cadmium in the amalgam the anode and the cathode potential became more electronegative. However in the cases where cathodic polarization was set up this dependence was observed only up to concentrations of 1-2 g-atoms of cadmium/liter of mercury in the amalgam, and with further increase of the cadmium concentration the potential reverses and then becomes more positive. We consider the cause of this phenomenon to be that at 1-2 g-atom of cadmium per liter of mercury a saturated solution is formed, and with further increase in the amount of cadmium in the amalgam crystals of metallic cadmium separate out, the crystals not being equally distributed throughout the amalgam, but are present in the form of aggregates (this actually occurred in our experiments).

The appearance of crystals in the amalgam causes an increase in the true surface of the mercury electrode (experiments involving sitrting) hence at one and the same current strength the c.d. is decreased, causing a displacement of the

1) In this and following tables the potentials are

TABLE 3

Dependence of the cathode and anode potential on the concentration of tin in the amalgam¹

Temperature (in. deg)												
48-53						78-83						
Current density												
0.044	0.055	0.07	0.09	0.11	0.0022	0.011	0.022	0.044	0.055	0.07	0.09	0.11
Cathode												
0.40	0.45	0.50	0.60	0.70	0.25	0.27	0.31	0.41	0.45	0.51	0.62	0.71
0.44	0.46	0.52	0.62	0.71	0.26	0.29	0.33	0.42	0.46	0.52	0.62	0.72
0.43	0.48	0.54	0.64	0.76	0.28	0.30	0.34	0.43	0.48	0.53	0.63	0.75
0.43	0.48	0.53	0.63	0.75	0.28	0.30	0.35	0.43	0.48	0.54	0.64	0.74
0.44	0.48	0.53	0.64	0.74	0.28	0.30	0.36	0.44	0.49	0.56	0.65	0.75
0.44	0.49	0.54	0.64	0.74	0.28	0.31	0.36	0.45	0.49	0.56	0.67	0.75
Anode												
0.11	0.07	0.02	+0.06	+0.16	0.27	0.24	0.20	0.11	0.07	0.02	+0.06	+0.16
0.11	0.08	0.02	+0.06	+0.14	0.26	0.24	0.20	0.10	0.06	0.01	+0.08	+0.17
0.12	0.08	0.03	+0.05	+0.14	0.27	0.24	0.20	0.12	0.08	0.02	+0.06	+0.15
0.13	0.09	0.03	+0.06	+0.14	0.28	0.24	0.21	0.12	0.08	0.01	+0.07	+0.17
0.12	0.08	0.02	+0.06	+0.16	0.28	0.26	0.21	0.11	0.07	0.01	+0.09	+0.18
0.12	0.08	0.03	+0.05	+0.14	0.28	0.25	0.20	0.12	0.08	0.03	+0.06	+0.15

potential towards more positive values.

With anode polarization, as the concentration of cadmium in the amalgam increases its concentration in the surface layers of the mercury electrode increases, hence the anode potential becomes more negative. Apart from this, as the concentration of cadmium in the amalgam increases crystals of metallic cadmium separate out, which increase the surface area of the electrode, and this in turn causes a lowering of the real c.d. and a displacement of the anode potential to more negative values.

The dependence of the cathode and anode potential on the temperature can be seen from the experimental data in Table 6.

As the temperature is raised the concentration polarization decreases and so does the hydrogen overvoltage, hence the cathode potential should become more positive, which is observed in the results. However at large concentrations of cadmium in the amalgam (8 g-atoms/liter of mercury) the cathode potential becomes more negative up to temperatures of 50°, and afterwards, with further increase of temperature, it becomes more positive. This is due as already noted, to the formation of crystals of metallic cadmium in the mercury amalgam. At lower temperatures the separation of these crystals leads to an increase of the surface of the mercury electrode, hence the potential becomes more positive because the true current density decreases. With increase of the temperature the solubility of the crystals of cadmium increases, the surface of the electrode decreases, and the potential becomes more electronegative. However this goes on as long as the whole of the cadmium existing as crystals does not dissolve in the mercury (for example at 50°) after which, with further increase in the temperature, the poten-

¹) In this and following tables the potentials are

TABLE 4

Experimental data on the deposition of cadmium on a mercury cathode

Initial con- centration of cadmium in the electrolyte (in g)	C.D. (in A/cm^2)	Potential (V)	Temp. (in deg)	Change in cathode potential (V) with time (mins.)													Current effici- ency (%)		
				0	4	8	12	16	20	24	28	32	36	40	44	48		52	56
L 136	0.11	6.6	20	1.22	1.29	1.33	1.46	1.53	1.54	1.56	1.56	1.56	1.56	1.56					27
L 136	0.11	5.1-5.7	50	1.12	1.16	1.22	1.38	1.48	1.54	1.54	1.54	1.54	1.54	1.54					32
L 136	0.055	4.3-4.5	20	0.88	0.92	0.98	1.16	1.23	1.30	1.32	1.32	1.32	1.32	1.32					54
L 136	0.055	3.9-4.2	50	0.76	0.80	0.84	1.10	1.23	1.30	1.30	1.30	1.30	1.30	1.30					65
2.272	0.11	6.2	20	0.94	0.98	1.06	1.32	1.50	1.54	1.57	1.58	1.58	1.58	1.58					46
2.272	0.11	5.8-5.6	50	0.92	1.0	1.06	1.36	1.48	1.54	1.54	1.54	1.54	1.54	1.54					65
2.272	0.055	4-4.4	20	0.63	0.69	0.74	0.80	0.84	0.92	1.16	1.26	1.33	1.35	1.35	1.36	1.36	1.36		51
2.272	0.055	2.5-4.1	50	0.54	0.62	0.74	0.72	0.80	0.82	0.99	1.20	1.27	1.29	1.29	1.29	1.29	1.29		72
5.68	0.11	6.2-5.8	20	0.86	0.88	0.94	1.02	1.08	1.12	1.15	1.33	1.45	1.51	1.56	1.57	1.58	1.58	1.59	62
5.68	0.11	5.2-5	50	0.80	0.83	0.93	1.0	1.06	1.11	1.12	1.30	1.46	1.50	1.54	1.54	1.54	1.54	1.54	81

TABLE 5

Experimental data on the decomposition of cadmium amalgams

Initial con- centration of cadmium in the amalgam (in g)	C.D. (in A/cm^2)	Potential (V)	Temp. (in deg)	Change of anode potential (V) with time (in mins.)													Current efficiency (%)		
				0	2	4	6	8	10	11	14	16	18	20	22	24		25	
1.136	0.11	3.1-6.2	20	+0.06	+0.03	+0.10	+1.06												108
1.136	0.055	1.4-2	20	0.20	0.18	0.17	0.15	0.14	0.11	+0.86									118
1.136	0.055	1 -1.5	50	0.20	0.20	0.20	0.19	0.18	0.15	+0.86									118
2.272	0.11	3.3-3.8	20	0.03	0.0	0.0	0.01	+0.03	+0.04	+1.06									118
2.272	0.11	2.3-3.4	50	0.05	0.01	0.0	0.0	+0.01	+0.03	+1.06									118
2.272	0.055	1.3-2.3	20	0.24	0.24	0.24	0.23	0.23	0.22	0.22	0.22	0.22	0.21	0.20	0.19	0.18	0.16	+0.31	104
2.272	0.055	0.8-1.5	50	0.24	0.23	0.22	0.22	0.22	0.22	0.22	0.22	0.21	0.20	0.20	0.19	0.18	0.17	+0.86	104

tial takes on a positive value as in all normal cases.

With anodic polarization, the diffusion of metal dissolved in the amalgam is more rapid at higher temperatures, and its concentration in the surface layers increases, so that the potential of the anode should become more negative. Actually it follows from the experimental data that when the temperature is raised, the anode potential becomes more positive. This may be connected, on the one hand, with the fact that the concentration of atoms of calcium in the surface layers of the amalgam decreases rapidly as the temperature rises at the expense of the cadmium dissolved in the sulfuric acid (local cells, the effect of which is not recorded on the ammeter), on the other hand there is possibly here a decrease in the degree of hydration of the ions with increase in temperature. We note that cadmium together with zinc is one of those metals the energy of hydration of whose ions is extremely high.

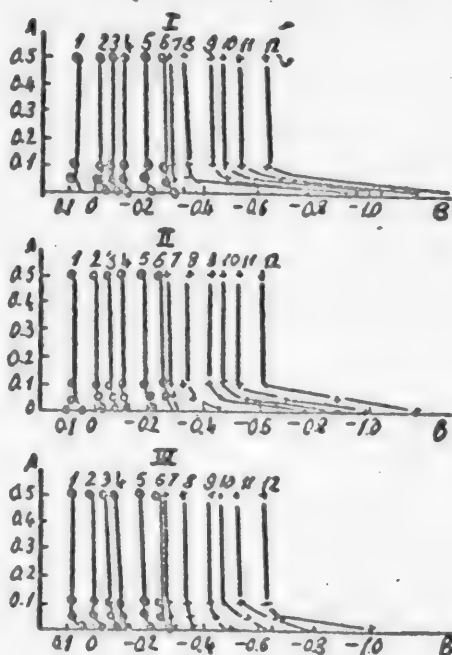


Fig. 1. Effect of concentration of tin in the electrolyte on the potential of the cathode and anode.

A - concentration of tin in the electrolyte (in g-ion/liter); B - potential of the anode and cathode (V).

Current density at the anode (A/cm^2):
 1 - 0.09; 2 - 0.07; 3 - 0.055; 4 - 0.044; 5 - 0.022; 6 - 0.0022. Current density at the cathode (A/cm^2): 7 - 0.0022; 8 - 0.022; 9 - 0.044; 10 - 0.055; 11 - 0.07; 12 - 0.09.

Temperature (in deg): I - 18-23; II - 48-53; III - 78-83.

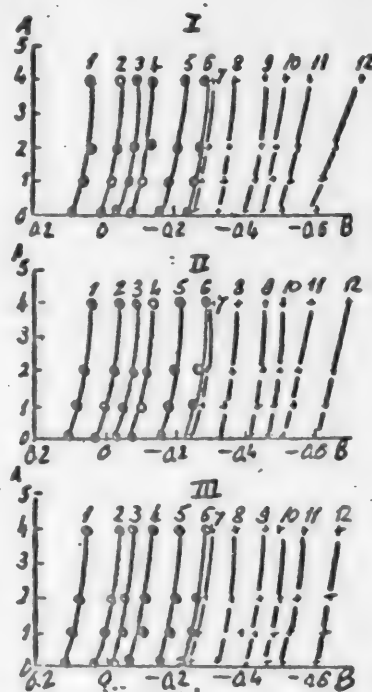


Fig. 2. Effect of acidity of the electrolyte on the cathode and anode potential.

A - normal electrolyte; B - Anode and cathode potential.

The figures on the curves have the same meanings as in Fig. 1.

Temperature (in deg): I - 18-23; II - 48-53; III - 78-83.

TABLE 6

Dependence of the cathode and anode potential on the concentration of cadmium in the amalgam

Concentration of cadmium in the electrolyte (g-atoms/liter)	Temperature (in deg)										
	18-23							48-53			
	Current density (in A/cm ²)										
	0.0022	0.011	0.022	0.044	0.055	0.07	0.09	0.11	0.0022	0.011	0.022
Cathode											
0.01	0.40	0.47	0.58	0.76	0.82	0.92	1.0	1.10	0.38	0.42	0.49
0.1	0.44	0.53	0.64	0.81	0.87	0.93	1.11	1.12	0.41	0.48	0.57
1	0.48	0.56	0.68	0.86	0.93	0.98	1.08	1.14	0.42	0.45	0.60
2	0.52	0.56	0.62	0.84	0.91	0.98	1.10	1.20	0.46	0.54	0.63
4	0.48	0.55	0.64	0.80	0.86	0.93	1.04	1.14	0.46	0.52	0.59
8	0.50	0.52	0.56	0.68	0.74	0.78	0.86	0.92	0.47	0.52	0.61
Anode											
0.01	0.40	0.36	0.32	0.24	0.20	0.16	0.08	+0.02	0.38	0.35	0.30
0.1	0.41	0.38	0.34	0.26	0.25	0.18	0.10	0.03	0.39	0.36	0.31
1	0.42	0.39	0.35	0.28	0.25	0.20	0.13	0.05	0.41	0.40	0.34
2	0.43	0.41	0.38	0.30	0.26	0.21	0.15	0.07	0.42	0.39	0.35
4	0.44	0.42	0.37	0.30	0.26	0.32	0.14	0.06	0.43	0.40	0.36

The dependence of the potentials on the current density can be seen from the data in Table 6.

From these it emerges that with increase in the c.d. the cathode potential becomes more negative but the anode more positive, and the higher the concentration of cadmium in the amalgam the greater the displacement towards the negative region. This excludes the displacement of potential at the concentration of 8 g-atoms of cadmium per liter of mercury at temperatures of 18-23° and 48-53°; the explanation of this has been given above.

The dependence of the anode and cathode potentials on the concentration of cadmium in the solution is shown in Fig. 3.

From these data it is seen that with increase in the concentration of cadmium in the electrolyte both the cathode and the anode potential become more positive, as in similar experiments with tin. However in the case of cadmium the course of the curves is more positive because cadmium is more electronegative than tin, and discharge potential of its ions is nearer than that of the tin ions to the discharge potential for hydrogen ions.

SUMMARY

1. From the experimental results are deduced the dependence of the cathode potential in the electrolytic deposition of tin and cadmium and of the anode potential in the electrolytic decomposition of tin and cadmium amalgams at different temperatures and different current densities on: a) concentration of metal in the amalgams; b) concentration of metal ions in the electrolyte; c) acidity of the electrolytes (for tin).

2. The possibility of decomposing the amalgams electrolytically has been established.

3. The need to take into account the physical state of the amalgam has been

TABLE 6

Dependence of the cathode and anode potential on the concentration of cadmium in the amalgam

Temperature (in deg)												
48-53						78-83						
Current density (in A/cm ²)												
0.044	0.055	0.07	0.09	0.11	0.0022	0.011	0.022	0.044	0.055	0.07	0.09	0.11
Cathode												
0.66	0.72	0.82	0.96	1.06	0.36	0.40	0.48	0.61	0.67	0.76	0.87	0.98
0.73	0.76	0.85	0.96	1.06	0.38	0.42	0.50	0.65	0.72	0.80	0.90	1.04
0.76	0.83	0.89	1.0	1.08	0.41	0.44	0.52	0.67	0.72	0.80	0.90	1.03
0.78	0.84	0.92	1.04	1.15	0.43	0.48	0.58	0.72	0.78	0.85	0.98	1.10
0.74	0.82	0.90	1.0	1.14	0.44	0.48	0.56	0.70	0.76	0.82	0.94	1.07
0.72	0.79	0.86	0.98	-	0.45	0.49	0.57	0.69	0.76	0.83	0.93	-
Anode												
0.23	0.18	0.14	0.06	+0.04	0.36	0.30	0.28	0.20	0.17	0.12	0.04	+0.06
0.24	0.20	0.16	0.08	+0.01	0.38	0.34	0.29	0.23	0.19	0.13	0.07	+0.06
0.26	0.22	0.18	0.11	0.03	0.40	0.38	0.32	0.25	0.21	0.16	0.10	+0.01
0.28	0.24	0.20	0.13	0.04	0.40	0.38	0.33	0.26	0.26	0.18	0.11	0.02
0.28	0.24	-	0.13	0.08	0.41	0.41	0.39	0.30	0.26	0.18	0.10	0.03

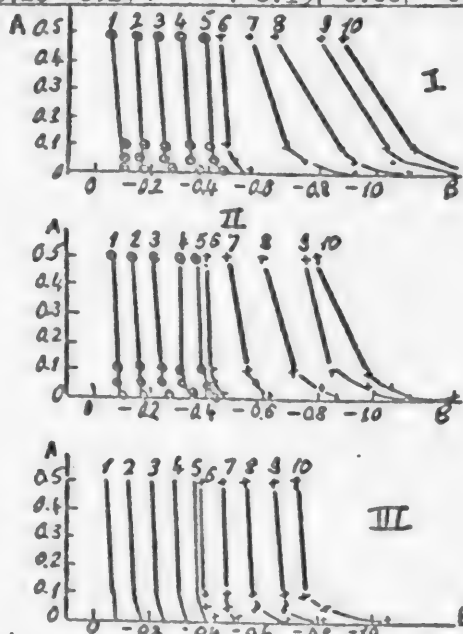


Fig. 3. Effect of concentration of cadmium in the electrolyte on the anode and cathode potentials.

A - concentration of cadmium in the electrolyte (in g-ion/l); B - anode and cathode potentials (V).

Anode current density (A/cm²): 1 - 0.09; 2 - 0.07; 3 - 0.044; 4 - 0.022; 5 - 0.0022; C.d. at the cathode (A/cm²): 6 - 0.0022; 7 - 0.022; 8 - 0.044; 9 - 0.07; 10 - 0.09. Temp. (in deg): I - 18-23; II - 48-53; III - 78-83.

noted, since with increase of concentration of metal in the amalgams the latter become more viscous, which causes a change in the surface area of the mercury electrode on stirring and a change in the real current density. Crystals may separate in the amalgam which change the surface area of the electrode to a different extent and as a result change the true current density, which is reflected in the magnitude of the potentials.

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SYNTHESIS OF MONOMERS AND PROPERTIES OF COPOLYMERS¹

B. H. Rutovsky and A. M. Shur

Polymethylmethacrylate is widely used but nevertheless suffers from a number of disadvantages. Its surface hardness and thermal stability are low and its chemical resistance insufficient. Polyallylmethacrylate, though having less of these deficiencies, is too brittle [1]; apart from this the polymerization of allyl methacrylate is so violent that it is difficult to keep it under control. Rutovsky and Zabrodina showed that the introduction of 10% allyl methacrylate into methyl methacrylate undergoing polymerization substantially improved the properties of the glass obtained.

The present work had the objective of finding out the effect of comparatively small additions of allyl and vinyl methacrylate on the properties of methyl methacrylate copolymers.

EXPERIMENTAL

Starting materials. The methyl methacrylate was colorless and transparent. The monomer was prepared immediately before experiment by distillation under ordinary pressure in a stream of nitrogen. The redistilled product boiled at 99-100° and had the following constants: specific gravity d_4^{20} 0.9444 and refractive index n_D^{20} 1.415.

Methacrylic acid was prepared from methyl methacrylate. The latter was treated with a small excess of caustic soda. A small quantity of ethanol was added to the mixture. The precipitate of sodium methacrylate was filtered, pressed on the filter, and afterwards decomposed with conc. HCl. The comparatively large amount of sodium chloride produced caused the methacrylic acid to be salted out. In specific cases salt was added to hasten this process. The upper layer consisted mainly of methacrylic acid containing a small quantity of water, while the lower one was a concentrated solution of sodium chloride.

The usual methods of drying the acid by different drying agents were useless, because the sample dried in this manner, on distilling rapidly stiffened (polymerized) and the loss of acid was very large. Dehydration was therefore brought about by azeotropic distillation of the water with the help of benzene. Methacrylic acid was then distilled over at 68-73° (15 mm Hg).

The amount of pure acid in the product obtained by distillation was determined by titration with alkali and came out at 98%; the bromine number was 192 (theoretical 186) and the n_D^{20} = 1.433.

Allyl alcohol was obtained from a mixture of glycerine and formic acid [2], the product being distilled and coming over at 195-260°. The alcohol was salted out with potash, dehydrated by boiling with anhydrous potash, and afterwards distilled under atmospheric pressure. The fraction coming over at 94-97° and having a refractive index n_D^{20} = 1.4125 was used for the synthesis of allyl methacrylate.

¹) Communication 1 of a series dealing with the copolymerization of methyl methacrylate with complex esters of unsaturated alcohols with methacrylic acid.

Benzoyl peroxide was recrystallized from alcohol after which it melted at 103°.

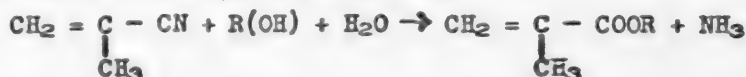
Hydroquinone was dissolved in water and boiled with active carbon, after which the hot solution was filtered and treated with SO₂. White crystals separated and were dried.

SYNTHESIS OF THE MONOMERS

Allyl methacrylate. We tested three methods given in the literature for the synthesis of esters: 1) alcoholysis of the nitrile of methacrylic acid; 2) transesterification; and 3) direct esterification.

1) Alcoholysis of nitrile of methacrylic acid. The starting material was acetone cyanhydrin, distilling at 80-83° (23-25 mm Hg). The colorless distillate had a refractive index of n_D^{20} 1.401.

This product was the starting material for obtaining the esters of methacrylic acid according to the scheme.



To test this method 20 g of hydroxynitrile was placed in a flask, together with 0.6 g of sulfur, (inhibitor) and 60 g of 1.81 H₂SO₄. In view of the extremely violent nature of the reaction, the acid was introduced in portions and the reaction mixture was cooled with water. 23 g of allyl alcohol were added to the darkened liquid along with 2 g of hydroquinone (inhibitor) and the mixture was boiled under reflux.

However allyl methacrylate was not obtained when the mixture was distilled. Experiments under other conditions gave no better results, so this method was abandoned.

2) Transesterification. This was done by heating an excess of alcohol with methyl methacrylate, sulfuric acid and hydroquinone.

In a flask connected to a condenser through a fractionating column and placed in an oil bath, an excess of carefully dehydrated allyl alcohol was added together with methyl methacrylate, sulfuric acid and hydroquinone. The allyl alcohol was in excess in relation to the methacrylate. When the temperature of the distilling vapour had reached 80° the process was interrupted and the contents of the flask distilled under vacuum. (43 mm Hg).

The fraction distilling at 59-61° was allyl methacrylate. The results of some of our experiments are shown in Table 1.

TABLE 1

Results of experiments on the preparation of allyl methacrylate by transesterification

Experiment Number	Charge				Allyl ester obtained (in g)	Yield of allyl ester (% of methyl methacrylate)	Remarks
	Allyl alcohol (g)	Methyl methacrylate (g)	Sulfuric acid, (% of charge)	Hydroquinone (% of charge)			
1	70	75	1	0.7	21	28	Addition of benzene to form an azeotrope.
2	122	136	1	0.7	14	10.3	
3	70	75	1	0.7	12	16	

The yield of allyl methacrylate by this method fluctuated within the limits of 10.6 and 28%. Such large fluctuations can be explained by the difficulty of regulating the temperature of the vapour leaving the fractionating column. The low yield is due to insufficiently sharp separation of the vapours in the column, as a result of which a considerable amount of allyl alcohol and of methyl methacrylate escaped from the flask before they had reacted.

Although we used this method in the first of our experiments, later on we prepared allyl methacrylate exclusively by direct esterification as in this method the yield was considerably higher.

3) Direct esterification of methacrylic acid with allyl alcohol. After boiling the mixture of allyl alcohol, methacrylic acid, sulfuric acid and hydroquinone for 6 hours, the products of reaction were washed 2-3 times with water (in a separating funnel), once with 10% NaOH, and then again once with water. After drying with calcium chloride the product was distilled under the same conditions as in the previous method, and the constants were practically the same. The results of certain experiments are shown in Table 2.

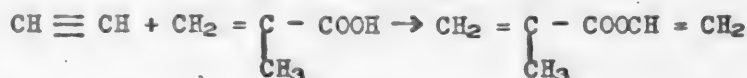
As can be seen from Table 3 the constants of the product obtained by direct esterification are close to those given in the literature.

TABLE 2

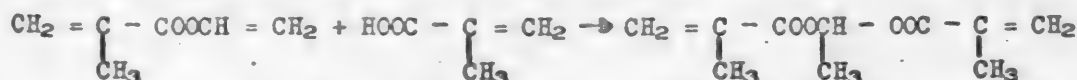
Results of experiments on the preparation of allyl methacrylate by direct esterification.

Expt. No.	Charge (in g)				Allyl ester obtained (g)	Yield of allyl ester (in % of the methacrylic acid)
	Methacrylic acid	Allyl alcohol	Sulfuric acid	Hydroquinone		
1	8.6	11	2	0.2	5	58
2	8.6	22	2	0.2	6	69.7
3	8.6	34.8	2	0.2	7.4	86.1

Vinyl methacrylate. Vinyl methacrylate was obtained by a method worked out by us analogous to the method used for obtaining vinyl acetate and a series of other complex vinyl esters and consisting in the passage of purified acetylene through methacrylic acid.



As in the synthesis of other complex vinyl esters, ethylene derivatives were formed in significant quantities, as a consequence of the interaction of the vinyl ester formed with the excess of acid:



The acetylene obtained from calcium carbide was purified by passage through a solution of sodium dichromate in sulfuric acid, a solution of alkali, and through a drying tower filled with calcium chloride. The last traces of hydrogen sulfide which might poison the mercury catalyst were removed by passing the gas through a column containing pumice soaked in copper sulfate and it was afterwards dried. The catalyst was obtained by dissolving mercuric oxide in methacrylic acid and mixing this solution with a solution of

orthophosphoric acid in methacrylic acid. As a result mercuric phosphate separated in a finely divided form, which ensured a large area of contact between it and the reacting mixture. To combine with the water of reaction (and with the water contained in the methacrylic acid), a calculated quantity of acetic anhydride was added to the reaction mixture. The removal of water with P_2O_5 was excluded by the fact that this would induce the formation of metaphosphoric acid, which would promote the formation of ethylene dimethacrylate. [4].

TABLE 3

Constants of the product, obtained by direct esterification

Physical property.	According to:		
	Rutovsky and Zabrodina [1]	Redberg [3]	Our own work
Refractive index	n_D^{18} 1.4389	n_D^{20} 1.4358	n_D^{20} 1.4370
Specific gravity	d_{20}^{20} 0.9351	d_{20}^{20} 0.9335	d_4^{20} 0.9339

The mixture of methacrylic acid and catalyst was mixed with a propeller type stirrer, through the follow shaft of which the acetylene was introduced. The shaft of the stirrer was connected to the source of acetylene through a special mercury seal. To prevent polymerization, 1% of hydroquinone was added (on the weight of the methacrylic acid). The quantity of acetylene passed through the acid at a temperature of 35-40° was

approximately 2 liters/hour and in toto was for example 0.8 g/g of acid. The general yield of the addition of acetylene to the acid under these conditions attained 80% on the weight of methacrylic acid.

Distillation of the products of addition of acetylene (after washing out the unreacted acid and drying) gave the results seen in Table 4.

The constants for fraction II were in pretty close agreement with calculated values (Table 5).

The bromine number was determined by the bromide-bromate method of Knopa [5] and the saponification was carried out with 5% aqueous alcoholic alkali in the cold.

The vinyl methacrylate obtained in this way was a colorless liquid with a small reminiscent of that of vinyl acetate, and was used for copolymerization with methyl methacrylate.

Investigation of some properties of the copolymers.

Copolymers with small contents of allyl and vinyl methacrylates were investigated, and some tests only were made on a copolymer with 10% of allyl ester.

Copolymerization was brought about by mixing the freshly prepared monomer with 1% of benzoyl peroxide. The prepared reaction mixture was heated on a water bath under reflux so as to obtain the so-called 'forepolymer' and the latter was poured into a glass mould prepared from two glass plates. After pouring, the opening in the mold was sealed up with thick paper. The polymerization was

TABLE 4

Results of distillation of the products of addition of acetylene

Fraction	Pressure (mm Hg)	Boiling range (in °)	Refractive index	Bromine No.	Specific gravity
I	150	40-61	1.4353	303	—
II	150	61-63	1.4377	264	0.9430
III	14	to 107 (97-107)	1.4395	247	—

TABLE 5
Comparison of the theoretical and observed constants for fraction II

Constants	Bromine No.	Saponification No.	Molar refraction
Theoretical	282	500	31.7
Obtained for fraction II	264	477	31.2
Deviation (%).....	6.4	4.6	1.1

carried on in a thermostat beginning at 40°, and after the material in the mold had lost its fluidity the temperature was raised to 65°. At this temperature the polymerization still took five days. To terminate the polymerization the mold was cooled to room temperature over a period of 2-3 hours. The methyl methacrylate polymer to compare with the copolymer was

prepared under the same conditions.

The samples were cut with a knife from the slates of copolymer so obtained and reduced to the right size by filing and rubbing with emery paper.

The resistance to the action of organic solvents was determined by extracting the samples with chloroform in a Soxhlet thimble for 6-8 hours (6 hours for the allyl, and 8 hours for the vinyl ester) and weighing the dried residue left behind after driving off the solvent from the extract. The impact and bend strength were determined by Dinstat's method; the hardness of the allyl methacrylate copolymer was determined on the Brinell and that of the vinyl methacrylate copolymer on the Rockwell scales.

The results of the tests are given in Table 6.

TABLE 6
Results of tests of the properties of copolymers

Property measured	Allyl methacrylate copolymer					Vinyl methacrylate copolymer			
	% allyl methacrylate in copolymer					% vinyl methacrylate in copolymer			
	0	10	15	20	40	5	10	15	20
Stability to organic solvents: Loss of weight (in weight %)	64.2	5.8	6.08	3.1	—	2.1	1.3	1.5	—
Thermal stability (°) (Vick)	116	126.5	132.5	141	—	—	—	—	—
Impact strength (kg.cm./cm ²)	17.3	17.1	22.3	18.8	21.2	12.62	12	11.45	—
Bend strength (kg/mm ²)	1268	1444	1333	1140	1042	1268	1415	1140	1115
Hardness (kg/mm ²)	18 ¹								
	24	25.9	25.9	28.4	—	26	28	30	—

As can be seen from Table 6, comparatively small additions of allyl or vinyl methacrylate markedly increase the stability of the polymers to organic solvents, copolymerization with the vinyl compound being more effective here than with the allyl compound: at the same time the thermal stability and the hardness are significantly increased as well. The impact and bend strengths of the

¹) Table 6. Upper figure = Brinell, lower figure = Rockwell hardness.

copolymers with allyl methacrylate differ to a small extent only from that of the pure polymer, while the co-polymer with vinyl methacrylate is somewhat deficient in respect of these properties.

Such a difference between the two copolymers is apparently connected with the fact that the structure of the trimeric macromolecule of the vinyl co-polymer is more rigid than that of the allyl methacrylate copolymer which increases the brittleness and the resistance of the polymer to solvents. The rigidity in its turn can be explained by the fact that the 'bridges' in the vinyl methacrylate copolymer, linking the linear macromolecules together, are shorter than in the allyl methacrylate copolymer, and their number per unit length is larger, as a consequence of which the reactivity of the vinyl group is raised relative to that of the allyl group.

Tests of the suitability of the copolymer for optical purposes. Only the copolymer with 10% of allyl methacrylate was examined. Side by side with the results of the examination of the copolymer are shown the results of tests of certain other analogous materials.

The refractive index of the copolymer with 10% of allyl methacrylate differs slightly from that of technical plasticized plexiglass (1.497) and from that of pure methyl methacrylate (1.490-1.492).

The change of the refractive index of the copolymer with temperature ($0.9 \cdot 10^{-4}$) is somewhat less than the figure for plexiglass molding powder ($1.1 \cdot 10^{-4}$) and of plexiglass without plasticizer ($1.0 \cdot 10^{-4}$).

The copolymer has a coefficient of linear expansion of $0.97 \cdot 10^{-4}$ which is very near to that of pressure cast plexiglass.

The thermal stability of the samples was determined as the depth of penetration of 2 mm balls under a pressure of 10 kg dead weight applied for 60 secs. The experiments were made in a thermostat at 20-130° and at each 10° in that interval. Temperatures at which the penetration was equal to 1 mm were found graphically.

The elasticity of the samples was determined on the same set up as that used for determining the thermal stability: it consisted in finding out the residual deformation 60 seconds after taking off the load.

The surface hardness was characterized by a lowering of the coefficient of reflection from the polished surface, as a result of the fall of 100 g of sand on to it from a height of 40 cms. The results are expressed in terms of the lowering of the coefficient of reflection (ΔK) as a percentage of its initial value.

The results of the experiments are set out in Table 7.

From them it can be seen that the copolymer is higher in thermal stability, temperature of maximum residual deformation, and surface hardness, than the samples of polymethylmethacrylate used for comparison.

SUMMARY

1) Methyl methacrylate copolymers containing up to 40% of allyl methacrylate are harder, more thermally stable, and have higher chemical resistance than polymethylmethacrylate.

2) Polymerized methyl methacrylate containing vinyl methacrylate has a higher resistance to organic solvents than that containing allyl methacrylate.

TABLE 7

Results of physical and mechanical examination of the copolymers

Samples	Thermal stability (T ₁₀₀)	Maximum residual deformation (as a fraction of the total deformation)	Temperatures of maximum residual deformation (°)	Surface hardness (ΔK)
Plasticized polymethylmethacrylate.....	81	0.8-0.9	80-85	31.5±3.0
Pressure molded polymethylmethacrylate.....	90	0.75-0.65	90	—
Unplasticized polymethylmethacrylate.....	95	0.75	100	31.7±2.0
Copolymer with 10% allyl methacrylate.....	121	0.6-0.65	105-110	13.4±2.0

3) The optical properties, impact, and bend strength of the copolymer with a small quantity of allyl methacrylate differ slightly from those for pure polymethylmethacrylate.

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CALCULATION OF THE VISCOSITY OF LACQUERS

I.R. Morozov

One of the characteristics of high molecular compounds is their viscosity. Lacquers, both on a nitrocellulose and an oil basis, are assessed by their viscosity which has to meet technical specifications; products of good quality may be obtained from sub-standard lacquers by changing the concentration, additions of other lacquers, etc.

The viscosity required by technical specifications relates to a quite definite temperature, but in practice this temperature is not always adhered to. Hence it is necessary to be able to establish the viscosity of lacquers at the temperature required by technical specifications, if the determination has been carried out at another temperature, and also, the viscosity of a mixture, as a function of the viscosities and quantities of the components.

This raises the need to work out the dependence of viscosity on a number of variables; temperature, concentration, and the nature of the solvent, the high molecular compound and the pigment. Many formulas are given in the literature relating the viscosity to a number of factors. We needed to select a formula in which there was a linear relation between some function of the viscosity and the independent variables as follows:

$$\frac{df(\eta)}{dx} = B \text{ or } f(\eta) = A + Bx,$$

where A and B are constants; x is the independent variable; and η is a function of viscosity.

A family of such relationships makes it possible to find easily a value of η for any value of x if A and B are accurately known beforehand. In particular cases the dependents may be more complicated. For example: $d \log(\eta)/dx$ may not be a constant but a function of x as follows:-

$$\frac{d \log(\eta)}{dx} = A + Bx$$

in particular cases

$$\eta = a (A + B \cdot bx)^x \quad (1)$$

$$\eta = a (e^n)^A + B \cdot bx \quad (2)$$

$$\eta = a (e^n)^{bx} (A + B \cdot bx^{\frac{+1}{-1}}) \quad (3)$$

$$\eta = a (e^n)^{eA + B \cdot bx} \quad (4)$$

$$\eta = a (e^n)^{e^{bx} (A + B \cdot b'x^{\frac{+1}{-1}})} \quad (5)$$

where x = the argument; η = viscosity; A and B = constants; e = base of natural logarithms; a and b are the scales on which the viscosity is calculated; a = viscosity scale, and b = argument scale. The scales and the value of n are so chosen as to make it convenient to calculate the viscosity on a slide rule. They

may be any arbitrary figures. These formulas express the changes of viscosity as a function of different parameters not only for lacquers but for many other liquids.

To illustrate what has been said, calculated values of viscosity are given in the tables below and are compared with experimental data taken from the literature. Under the columns of calculated viscosity are shown the formulas from which the viscosity was calculated and the numerical values of the constants A and B, of the scales a and b, of n, and the sign before unity if the viscosity was calculated from Formula (5).

TABLE 1

Expt. No.	Glycerine solution			Glycol solutions			Glycogen solutions		
	Concentration	Viscosity		Concentration	Viscosity		Concentration	Viscosity	
		Observed	Calculated		Observed	Calculated		Observed	Calculated
1	100	110	110	14.11	1.40	1.40	20	4	3.85
2	95	38	36	33.4	1.67	2.22	25	5	4.5
3	90	17	17	45.13	3.16	3.16	30	7	6.4
4	85	8.9	8	49.55	3.62	3.67	35	11	11
5	80	5.4	4.8	60.43	4.75	4.95	40	20	22
6	75	3.6	3.4	69.5	6.95	7.00	45	60	60
7	70	2.6	2.6	75.64	9.05	9.00	—	—	—
8	—	—	—	100	20.0	20.0	—	—	—
Formula			(5)			(5)			(5)
A....			14			9.4			15.66
B....			1200			0.2			- 160
a....			1			1			1
b....			1			1			1
n....			0.1			0.1			0.1
Sign...			—			+			—

In Table 1 values of viscosity calculated as a function of concentration are compared with experimental data for the viscosity of glycerine solutions (from Ubbelohde [1]), glycol (Dunstan [2]), glycogen (Bottazzi and d'Errico [3]); in Table 2 are given the values for solutions of pseudoglobulin (Chick [4]) and a suspension of sulfur (Oden [5]).

In Table 3 calculated values of viscosity for different temperatures are compared with experimental data for the viscosity of caustic soda and potash, sodium phosphate and boric oxide (Arndt and Polets [6]); in Table 4 the same is done for ethanol and a 60% solution of beet sugar (Bingham [7]), bismuth chloride (Aten [8]) and castor oil (from the 'Technical Encyclopedia').

This is repeated in Table 5 for the viscosity of carbon disulfide, ethanol, and glycerine as a function of pressure (Bridgman [9]); and for castor oil (from the 'Technical Encyclopedia'). It can be seen from these tables that the viscosities of liquids as a function of concentration, temperature and pressure calculated by formulas agree with quite sufficient accuracy with experimental data. The dependence of the viscosity of liquids of homologous series can also be expressed with similar accuracy. Thus, for example, the curves for the change of viscosity of saturated hydrocarbons as a function of the molecular weight and specific gravity can be expressed by the formula:

$$\eta = 0.1 [e + 0 \cdot (M \cdot d)]^{0.02 \cdot M \cdot d}$$

i.e. Formula (1) where $\underline{A} = \underline{e} = 2.72$; $\underline{B} = 0$

TABLE 2

Expt. No.	Solution of pseudoglobulin			Suspension of sulfur				
	Concentration	Viscosity		Concentration	Viscosity			
		Observed	Calculated		Particles of diameter 100 μ		Particles of diameter 10 μ	
					Observed	Calculated	Observed	Calculated
1	6	1.82	1.73	10	1.14	1.14	1.20	1.22
2	8	2.22	2.24	20	1.36	1.39	1.70	1.60
3	10	3.15	3.15	30	1.86	1.82	2.50	2.30
4	12	4.5	4.5	40	2.58	2.52	3.96	3.55
5	14	7	7	50	3.70	3.70	5.75	5.75
6	16	12	12	—	—	—	—	—
7	18	22	22	—	—	—	—	—
8	20	40	45	—	—	—	—	—
Formula...			(5)			(1)		(1)
Values of:								
A..			2.71			1.1		1.17
B..			0.14			0.04		0.05
a..			1			1		1
b..			1			0.1		0.1
n..			0.1			—		—
Sign.....			+			—		—

The curves of change of viscosity of aliphatic acids is expressed by the formula:

$$\eta = 0.1 \cdot (e^{0.1}) e^{M \cdot d} / (7.5 + 0.2 \cdot M)$$

i.e., Formula (5), where \underline{M} = molecular weight and \underline{d} = specific gravity of the compound.

\underline{A} and \underline{B} can be calculated from the viscosities of the liquids, at two different values of the argument, by substitution and solution of the equations.

Viscosity of lacquers. In the tables given below the observed and calculated viscosities of solutions of different lacquers mainly as a function of concentration, pigment content, and temperature, are compared.

In Table 6 the values of viscosity as a function of concentration of solutions of castor oil, and of resins FB-2 and 132 in benzene, are set forth; and in Table 7 the viscosities of solutions of pervinyl chloride resins in solvent naphtha, of polyvinyl chloride resins in acetone-butyl acetate-toluene (3:3:4) and of gelatin in water.

In Table 8 are given the viscosities of a thick paint as a function of its oil content and of DMSA, AP-Aluminic, and FB-2 lacquers as a function of their aluminum powder content; while in Table 9 will be found data for the viscosity of the nitrodope EM-white (prepared from nitrocellulose of different viscosities)

and of pigmented dope AS-30 as a function of its pigment content.

In the Tables the type of viscosimeter which was used for determining the viscosity is mentioned. As would be expected, both the values of the constants and the formula for calculating the viscosity depend on the nature of the solution and the type of viscosimeter. At present the viscosity of nitrocellulose is determined in 2% acetone solution in an Engler viscosimeter; the viscosity of varnishes is determined in other viscosimeters. Hence cases frequently arise where a nitrocellulose appears quite suitable for use (according to technical specifications) but the lacquer made from it may have to be discarded.

TABLE 3

Expt. No.	Temp. (in °)	Viscosity							
		NaOH		KOH		Sodium phosphate		B ₂ O ₃	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	350	4	4						
2	400	2.8	3	2.3	2.3				
3	450	2.2	2.3	1.7	1.8				
4	500	1.8	1.8	1.3	1.3				
5	550	1.5	1.5	1.0	1.0				
6	600			0.8	0.8				
7	650					1250	1300		
8	700					700	725		
9	750					470	470	34000	32000
10	800					300	300	26000	28000
11	850					210	210	17000	18000
12	900							11800	12000
13	1000							7000	7800
14	1100							4000	3800
Formula.			(4)		(4)		(4)		(4)
Values of:									
A.			4.125		4.44		5.425		5.18
B.			-0.0015		-0.0011		-0.0015		-0.00144
a.			0.1		0.01		1		1
b.			1		1		1		1
n.			0.1		0.1		0.1		0.1

Apart from this it is not unnecessary to mention that the viscosities of solutions of nitrocellulose differing in specific viscosity and in origin (i.e. nitrogen content) change to a different extent in going from one solvent to another.

In Table 10 are set forth the average coefficients of change of viscosity of solutions of three samples of nitrocellulose when transferring from butyl acetate to solvents ASH-30, AGT and DM (at different concentrations). With increase in the concentration of the solutions the coefficient of change of viscosity changes differently, according to the nature of the cellulose sample. This is apparently connected with the structure of the nitrocellulose molecules.

From all this it follows that the suitability of nitrocellulose as a lacquer base for one or other varnish may be assessed with least error only by determining its viscosity in solvents and in the concentrations in which the

given lacquer will be used; if the coefficient for the conversion of the viscosity figures determined in one viscosimeter to those that would be obtained with another is not known, then the viscosity of the solution must be determined in the same viscosimeter as is used for checking the lacquer itself.

TABLE 4

Expt. No.	Temp. (in °)	Viscosity						Temp. (in °)	Viscosity of bismuth chloride	
		Solution of beet sugar		Castor Oil		Ethanol			Observed	Calculated
		Observed	Calculated	Observed	Calculated	Observed	Calculated			
1	0	238	240	7200	7200	1.77	1.77	260	32	32
2	10	100	110			1.50	1.50	270	29	30
3	20	56.5	56.5	1000	1100	1.20	1.25	280	27	27.5
4	30	33.8	33			1.00	1.05	290	25	25
5	40	—	—	221	246	0.83	0.86	300	23	24
6	50	21.3	20			0.7	0.72	310	21	22
7	60	9.8	9	80	80 ^v	0.47	0.46	320	20	21
8	70	7.15	6.7					330	19	19.5
9	80	5.4	5.2	35	30			340	18	18
10	90	4.15	4.0							
11	100	3.34	3.34	17	15					
Formula			(4)		(4)		(2)			(2)
Values of:										
{ A			4		3.9		2.88			5.27
{ B			-0.015		-0.008		-0.008			-0.007
{ a			1		0.1		0.1			1
{ b			1		1		0			1
{ n			0.1		0.1					

TABLE 5

Expt. No.	Pressure (atm)	Viscosity						Pressure (atm)	Viscosity of castor oil	
		Carbon disulfide		Ethanol		Glycerine			Observed	Calculated
		Observed	Calculated	Observed	Calculated	Observed	Calculated			
1	1	0.35	0.39			3.8	3.8	1	197	197
2	500	0.44	0.44	0.559	0.56	5.2	4.7	24	263	265
3	1000	0.51	0.49	0.585	0.59	6.9	6.0	227	437	420
4	2000	0.81	0.61	0.654	0.66	11.8	10	550	682	650
5	4000	1.13	0.95	0.785	0.82	32	27	864	980	980
6	6000	1.65	0.50	0.957	1.00	84	74	1164		
7	8000	2.42	2.30	1.192	1.30	200	200			
8	10000	3.60	2.55	1.525	1.60	515	550			
9	12000	5.30	5.50	1.962	1.90					
Formula			(2)		(2)		(2)			(2)
Values of:										
A			1.37		1.665		1.3			5.25
B			0.022		0.011		0.05			0.00142
a			0.1		0.1		0.1			1
b			0.01		0.01		0.01			1

With increase of concentration the viscosity of the colloid solutions increases more, the more marked the tendency of the solutions to gelatinize, as is evident from the formulas and the constants for the change of viscosity of solutions of per- and polyvinylchloride resins and gelatin solutions (Table 8). The gelatin solutions have the largest and the pervinylchloride solutions the smallest tendency to gelatinize. This is also confirmed by the change of viscosity of DMSA, AP-aluminic and FB-2 as a function of their aluminum powder content (Table 8). FB-2 has the largest tendency to gelatinize.

TABLE 6

Expt. No.	Concentration (%)	Viscosity of Solutions (Secs.)							
		Castor oil		Resin FB-2		Resin No 132		Resin No 32	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	100	80	82	3300	3300				
2	90	28	30	980	1000			2300	2350
3	80	12	11	300	310	1700	1700	500	520
4	70	6	6	106	110	490	500	135	136
5	60	4	3.5	38	40	163	160	37	35.5
6	50	2.5	2.5	15	16.2	52	56	10	11
7	40	2	1.9	8	7.5	21	20	4	4.2
8	30	1.5	1.7	4	3.7	8	8.3	2	1.9
Formula			(5)		(1)		(1)		(1)
Values of	A		1.36		1.25		1.73		0.67
	B		0.078		0.1		0.1		0.19
	a		1		1		1		1
	b		0.1		0.1		0.1		0.1
	n		0.1						
Sign			+						
Type of viscosimeter		FE ¹ (5 mm)		FE (5 mm)		FE (4 mm)		NIILK (7 mm)	

The viscosity of GM-white nitro-dope (Table 9) as a function of its pigment content increases differently according to the origin of the nitro-cellulose. The viscosity of dope from less viscous nitrocellulose may be higher than that from more viscous. This may also be observed with pigmented dopes.

Investigation of the viscosity of lacquers as affected by variation of temperature between summer and winter. The lacquers placed in closed cans, were mounted in banks on an agitator in thermostat at different temperatures. The viscosity determinations were carried out when the temperatures of the lacquers became identical with that of the thermostat. The viscosity figures obtained are set forth in the tables; in Table 11 are the viscosities of nitro-dope and in Table 12 those for oil varnishes. The observed viscosities are compared with those calculated from formulas. The agreement is sufficiently accurate.

Using the formulas thus determined and checked, we can calculate the coefficient for converting viscosities at various temperatures to 18-20° and also for converting viscosities in one viscosimeter to those in another. The coefficients thus calculated are used satisfactorily in our factories.

¹⁾ FE here and elsewhere means the Ford-Engler viscosimeter; the diameter is indicated in brackets.

TABLE 7

Expt. No.	Solutions of pervinylchloride resins			Solutions of polyvinylchloride resins			Solutions of gelatin		
	Concentration (%)	Viscosity (in sec)		Concentration (%)	Viscosity (in sec)		Concentration (%)	Viscosity (in sec)	
		Observed	Calculated		Observed	Calculated		Observed	Calculated
1	6	4	4.1	17	3	3.1	6	1	1.1
2	8	7	7.3	19	4	4.3	7	2	1.8
3	10	12	13.5	21	6	6.4	8	3	2.9
4	12	26	27	23	10	10	9	4	4.3
5	14	52	55	25	22	20	10	8	8.2
6	16	130	120	27	40	44	11	19	18
Formula			(1)			(5)			(5)
Values of	A		1.215			6.35			3.6
	B		0.0083			0.04			-0.03
	a		1			1			1
	b		1			1			1
	n					0.1			0.1
Sign						+			+
Type of viscosimeter		FE (5 mm)							

TABLE 8

Thick paint.			Quantity of Al powder (in g/100g of paint)	Viscosity of enamel					
Oil content	Immersion depth: concentration (%)			DMSA		AP-Al		FB-2s	
	Observed	Calculated		Observed	Calculated	Observed	Calculated	Observed	Calculated
30	5	5	5	16	16.5	15	14.6	30	30.4
35	7	7.5	10	25	26	22	21	37	37.4
40	11	11.2	15	40	39	29	29.5	45	46.5
45	15	17	20	55	57	43	45	61	60.6
50	25	25	25	80	80	55	54	82	80
55	37	37.5	30	105	110	70	72	110	109
			40	200	195	124	120	225	230
			45	250	250	155	155	360	360
Formula		(2)			(3)		(3)		(3)
Values of	{	A	-0.83		9.5		12.7		2.73
		B	0.081		0.1		0.083		-0.023
		a	1		10		10		25
		b	1		1		1		1
		n			1		1		0.1
Type of viscosimeter - Conical. Load 30g				FE (5 min)					

Properties of the formulas derived. A very practical and important property of the formulas derived is that the average figure for the sum of the numerators

or denominators corresponds to the average figure for the sum of the values of the argument.

For example: from Table 1 $\log \log \eta$ for glycerine at a concentration of 85% is equal to half the sum of ($\log \log \eta$ for 100% concentration + $\log \log \eta$ for a concentration of 70%); from Table 2 (col.7) the denominator of the viscosity of a sulfur suspension at 30% concentration is equal to the average value of the sum of the denominators at 10 and 50%. As a result of this the viscosity of mixed dope may be calculated from the viscosity and concentration of the initial dope from the following formula:

$$\eta = \frac{\left[q \cdot \eta_1^{\frac{1}{C_1}} + d \cdot \eta_2^{\frac{1}{C_2}} + v \cdot \eta_3^{\frac{1}{C_3}} \right]^C}{q + d + v}, \quad (6)$$

$$\eta = e^{\frac{(q \log \eta_1 + d \log \eta_2 + v \log \eta_3)}{q + d + v}} \quad (7)$$

$$\eta = (e^n)^e \quad (8)$$

where η = viscosity of the mixed lacquers; η_1 , η_2 and η_3 = viscosities of the lacquers; C_1 , C_2 and C_3 = concentration of initial lacquers; C = concentration of mixed lacquers; q , d and v = quantities of initial lacquers.

Formula (6) is used when the change of viscosity is expressed by Formula (1), Formula (7) when the change is expressed by Formulas (2) and (3) and formula (8) when the viscosity is expressed by Formulas (4) and (5).

TABLE 9

Expt. No.	Quantity of paste (in g/100g of base)	Viscosity of nitrocellulose used (Engler)						Viscosity of pigmented dope ASH-30	
		1.10		1.19		1.13			
		Viscosity of nitrocellulose enamel DM-white (sec)							
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	10	12	11.8	10		18	18		
2	30	16	16.9	11	11.05	23	22.5		
3	50	27	25.8	12	12	24	24		
4	70	40	41.5	13	13.2	25	24.8	86	87
5	90	74	74	15	14.8	25	25.4	110	109
6	110							140	138
7	130							176	179
Formula			(3)		(3)		(3)		(3)
Value of	{ A B a b n		6.3		33.5		7		0.91
			-0.02		-0.117		1		-0.0043
			10		10		10		39
			1		1		1		0.1
			0.1		0.1		0.1		0.1
Type of viscosimeter		FE (5 mm)							

TABLE 10

Expt. No.	Viscosity of nitrocellulose (Engler)	Coefficients of change of viscosity of solutions with the solvents		
		ASH-30	AGT	DM
1	1.24	1.35	1.4	1.23
2	1.18	1.32	0.93	Smaller the higher the concentration
3	1.03	Larger the higher the concentration	1.0	0.9

TABLE 11

Expt. No.	Temperature (C°)	Viscosity of nitrocellulose dope of different trade marks (sec)									
		AMT-P		AMT-K		AK-20		A-1-H		ASH-30	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	-10	45	44	220	220	220	220	600	600	30	29
2	-5	30	33	170	165	185	180	450	440	20	20
3	0	22	23	120	120	150	150	357	360	15	14
4	5	20	18	100	100	115	110	275	270	10	97
5	10	15	14	80	81	92	90	223	220	6	6.5
6	15	12	11	65	67	72	74	175	180	5	4.5
7	20	9	9.5	57	55	60	59	150	150	3	3.1
8	25	8	7.8	45	44	50	52	110	110	2	2.1
9	30	7	6.7	35	36.5	45	43	100	100		
10	35	6	5.8	31	30	35	37	75	76		
11	40	5	5	27	27	32	32	67	67		
Formula		(4)		(4)		(4)		(4)		(2)	
Value of	A	3.45		3.88		3.9		4.075		2.625	
	B	-0.017		-0.01		-0.009		-0.0088		-0.075	
	a	1		1		1		1		1	
	b	1		1		1		1		1	
		n		0.1		0.1		0.1		1	
Type of viscosimeter		FE (5 mm)						Conical			

The amount of initial dopes for obtaining the mixtures with the specified viscosity is calculated by solution of the following equations:

$$\alpha \cdot \eta^{\frac{1}{C}} = x \cdot \eta_1^{\frac{1}{C_1}} + (\alpha - x) \cdot \eta_2^{\frac{1}{C_2}}, \quad (9)$$

$$e^B = e^{[x \log \eta_1 + (\alpha - x) \log \eta_2] / \alpha} \quad (10)$$

$$(e^n)^{e^B} = (e^n)^{e^{[x \log \log \eta_1 + (\alpha - x) \log \log \eta_2] / \alpha}} \quad (11)$$

where α = quantity of dope of specified viscosity; x = unknown quantity of one of the initial dopes; B = logarithm of the specified viscosity; η_1, η_2, η_3 = viscosities of the specified and initial dopes; and C_1, C_2 and C_3 concentrations of the specified and initial dope.

TABLE 12

Expt. No.	Temperature (°C)	Viscosity of dopes of different marks (sec)							
		Castor Oil		Drying Oil		Export. Lacquer		FB-2	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	-10	-	-	65	66	117	115	117	120
2	-5	180	180	40	38.5	70	68	70	73
3	0	113	110	25	25	45	45	50	50
4	5	80	82	18	17.5	31	30.5	30	33
5	10	54	55	12	12.2	20	21	25	24.5
6	15	40	42	9	9	16	15	20	1
7	20	35	33	8	7	12	115	13	13.5
8	25	25	24.5	5	4.75	9	9	11	10
9	30	20	18	4	4.5	7	7.2	8	8.4
10	35	15	15	4	3.8	6	575	7	6.8
11	40	12	12	3	3.2	5	4.9	6	5.7
Formula			(4)		(4)		(4)		(4)
Values of		A	3.86		3.47		3.64		3.66
		B	-0.016		-0.025		-0.022		-0.02
		a	1		1		1		1
		b	1		1		1		1
		n	0.1		0.1		0.1		0.1
Type of viscosimeter.		FE (5 mm)							

TABLE 13

Expt. No.	Viscosity of initial solutions		Ratio of solutions in mixture	Viscosity of mixture (in sec)	
	Solution 1	Solution 2		Observed	Calculated
1	22	69	1:1	39	40
2	22	108	1:1	53	50
3	22	165	1:1	60	64
4	22	1100	1:1	185	188
5	69	108	1:1	92	90
6	69	165	1:1	108	110
7	69	1100	1:1	285	280
8	108	165	1:1	128	130
9	108	1100	1:1	350	360
10	165	1100	1:1	450	440
11	22	1100	1:2	330	330
12	22	1100	2:1	92	90
FE viscosimeter			(5 mm)		

All these formulas apply to dopes prepared from materials of different viscosities. In Table 13 are set forth observed and calculated figures for the viscosities of solutions obtained by mixing solutions of nitrocellulose of different specific viscosities; the calculated values were obtained from Formula (6). The solutions were prepared at 13% concentration in ASH-30 solvent (imported nitrocellulose). As can be seen, the experimental viscosity is in quite good agreement with the calculated one.

Effect of form of viscosimeter, diameter of opening and concentration on the flow of solutions of castor oil in dibutylphthalate. Since the change in the viscosity of liquids as a function of different variables is expressed by the different formulas presented, it was interesting to investigate the rate of flow of liquids from vessels of different shapes as a function of the diameter of the opening.

TABLE 14

Concentration of solution	Diameter of aperture											
	2		3		4		5		6		7	
	Time of flow (in secs)											
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
0	105	105	66	66	41	41	25	25	16	16	10	10
20	140	137	80	83	50	48	28	27	18	17.5	11	11
40	205	206	120	121	65	64.5	40	37.2	22	22.4	14	14
60	350	348	195	197	100	100	55	54	32	32.3	20	20.2
80	680	670	350	357	180	176	95	94	55	54	33	33.5
100	1560	1580	728	725	360	352	190	187	100	99.5	62	62
Formula		(1)		(1)		(1)		(1)		(1)		(1)
Values of	A	1.097		1.095		0.040		1.010		1.012		1.012
	B	0.0214		0.0117		0.020		0.0213		0.0188		0.0188
	a	105		66		41		25		16		10
	b	0.1		0.1		0.1		0.1		0.1		0.1

TABLE 15

Dia- meter of aperture	Concentration of solution												
	0		20		40		50		80		100		
	Time of flow (in secs)												
	Ob- ser- ed	Cal- cu- lated	Ob- ser- ved	Cal- cu- lated	Ob- ser- ved	Cal- cu- lated	Ob- ser- ved	Cal- cu- lated	Ob- ser- ved	Cal- cu- lated	Ob- ser- ved	Cal- cu- lated	
2	105	105	140	138	205	210	350	360	680	695	1560	1520	
3	66	66	80	83	120	118	195	188	350	346	728	730	
4	41	41	50	48.2	65	66.7	100	102	180	182	360	362	
5	25	25	28	29.2	40	38.8	55	57	95	97	190	190	
6	16	16	18	17.7	22	23	32	32	55	55.5	100	105	
7	10	10	11	11	14	14	20	20	33	33	62	62	
Formula		(1)		(1)		(1)		(1)		(1)		(1)	
Values of	{	A	1.60		1.61		1.62		1.63		1.64		1.65
		B	0.00		0.01		0.02		0.03		0.04		0.05
		a	10		11		11		20		33		62
		b	1		1		1		1		1		1

Cans were made from sheet iron. The thickness of the cans was 0.45 mm, their height 4.5 cms, and their diameter 7.5 cms. Holes of the following diameters were made in the floors of the cans: 2, 3, 4, 5, 6, and 7 mm. Solutions of castor oil in dibutylphthalate were poured in. While the cans were being filled the holes were closed, and they were opened again at the same time as a stop watch was started. The latter was kept going until 190 cm³ had flowed out. Several determinations of the time of flow were made. The temperature of the solutions was 19.5-20°. The results of determinations are set forth in Tables 14-15.

The flow times of solutions as a function of the concentration are expressed by Formula (1) and also as a function of the diameter of the opening by an obvious change of Formula (1):

$$t = a[A + B(7 - \Delta)]^{7-\Delta}, \quad (12)$$

where t = time of flow and Δ = diameter of opening. The rate of flow of water from these tins as a function of the diameters of opening is expressed by Formula (1). The values of the constants are as follows: $A = 1.28$; $B = 0.05$; $a = 15$; $b = 1$. The results of the determinations are set forth in Table 16.

TABLE 16

No. of Expt.	Diameter of opening	Rate of flow of water (secs)	
		Observed	Calculated
1	2	125	124.5
2	3	70	72
3	4	45	44
4	5	30	28.5
5	6	20	20
6	7	15	15

SUMMARY

1) It has been shown that the dependence of the viscosity of dopes and varnishes on different variables may be expressed by formulas of the type:

$$\frac{df(\eta)}{dx} = \text{const and } \frac{df(\eta)}{dx} = f(x).$$

2) The values of the constants expressing $f(\eta)$ as a function of the independent variables have been determined. The values of the

constants were calculated for different viscosimeters and for different conditions (temperature, concentration, etc).

3) It has been shown that these formulas can be used in practice.

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METHOD OF ANALYSIS OF PLANT SUBSTANCES

E. V. Kondratiev and M. I. Kostina

Dept. of General Chemistry of the Moscow Medicinal Institute

One of us has already shown that when determining lignin in certain lower plants by separating it from them with concentrated mineral acids, high results are obtained, which is explained by the supposition that part of the pentosans are thereby transformed into non-hydrolyzable substances, which are determined with the lignin [1]. The aim of the present work has been the more detailed study of this question, which is of primary importance for obtaining accurate information about the composition of plant substances. We do not dwell here on the effect of the carbohydrate complex as a whole on the determination of the yield of lignin, because a positive and unique answer has been given to this by many investigators; nowadays it is considered essential in the analysis of plant substances to extract the hemicellulose from them before isolating the lignin residue. However, there are a series of points which have still not been studied, namely the complete extraction and the possibility of converting part of the carbohydrates to non-hydrolyzable substances by the action of dilute acids. It has been established that not all pentosans are easily hydrolyzed under these conditions. Usually this part of the pentosans is included in the determination of the cellulose, which negates the possibility of their condensation by further treatment with concentrated acid. It is not clear whether the pentosans alone are not completely hydrolyzed by dilute acid or whether other component parts have the same property. Furthermore, other methods of isolating lignin from the plant complex are known, in particular that based on treatment of the initial material with alkali whereby both hemicellulose and lignin are extracted and these are separated from one another by subsequent repeated precipitations and solutions of the lignin in alkali and alcohol [2]. However, in the final analysis this method is not achieved without the use of acid at elevated temperatures, avoiding many of the questions posed above. Their complete solution is a very responsible and difficult task and we do not pretend to achieve it in this paper. However, the experimental material we have obtained does permit us in spite of everything, to illuminate some points of the analysis.

EXPERIMENTAL

The process of extraction of hemicellulose with acids was studied in relation to the hydrolysis of three forms of plant: pinewood, a grass (*Eriophorum vaginatum*), and sphagnum moss. They were analyzed by the method described previously [1], in which the only change was that the extraction of the easily hydrolyzed hemicellulose was produced by heating on a boiling water bath with 1 N hydrochloric acid for 5 hours. By changing the concentrations and times we found that the conditions given ensured the maximum yield of reducing substances and did not affect the quantitative determination, by later hydrolysis with concentrated sulfuric acid, of the cellulose and lignin. All the analytic data reported here were checked by duplicate experiments. In Table 1 are shown the contents of the components studied.

On the other hand the residue from the hydrolysis by 1 N HCl was subjected to reaction with 12% HCl, after which the cellulose and lignin were also

determined in it.¹ The results of analysis are given in Table 2.

It is quite evident that in all samples the cellulose fraction is almost quantitatively divided among the substances decomposable by 12% HCl and by concentrated sulfuric acid; the lignin residue varied from 0.62 in pinewood to 4.39 in the grass and 4.33% in the moss.²

This shows that, particularly in the two latter materials, the carbohydrate takes an active part in the formation of lignin even where the main part of the lignin has been extracted by preliminary treatment with dilute acids: the polyuronic complex is more active than the pentosans in this respect. We compared two preparations of the grass lignin; one obtained by the usual method, the other by preliminary decomposition with 12% HCl followed by methylation of the hydroxyl group with dimethyl sulfate in alkaline solution³, and of the carboxyl group with methanol saturated with hydrogen chloride. Results are presented in Table 3.

As can be seen, the extraction of pentosans from the plant substance and the elimination of the carboxyl group produces substances with a considerably smaller number of peripheral groups, and a considerable rise in the initial methoxyl content. Turning our attention to the absence of carboxyl groups in the second preparation, the question arises as to whether the uronic acid does not owe its existence to the carboxyl group usually determined in the lignin. Actually even after hydrolysis by concentrated sulfuric acid directly on the lignin residue, the yields of which are shown in Table 1, we found a considerable quantity of uronic acids and a somewhat smaller quantity of pentosans, as shown in Table 4.

Re-calculating the data on the basis of the mass of lignin, we see that the content of foreign matter which is usually not taken into account in the analysis of plant substances comprises, in %: for wood, 7.41, grass 9.86, and moss 16.05. It would be erroneous however to suppose that the introduction of this one correction would completely solve the problem of determining the lignin, because the carbohydrate may in part not be preserved during the determination but may, as a result of condensation, actually participate in the formation of lignin.

The uronic acids are peculiar in that, splitting off carbon dioxide, they are converted to pentoses and only partly decomposed to furfural; as is known the latter is obtained from galacturonic acids in yield of 43.08% and from glucuronic acids in 39.38% of the possible theoretical yield [3]. From this point of view it appeared to us expedient to study, under the conditions of separation of lignin by concentrated sulfuric acid, the behavior of separate complex carbohydrates and in the first instance, of the polyuronide complex.

This was prepared by oxidation of pure cellulose and analyzed. Carbon dioxide was not produced by treating it with 1 N HCl, and sulfuric acid decomposed only 20.92% of it relative to the polyuronic acids in the initial complex; however, it was not possible to discover the formation even of traces of furfural. Thus 79.08% of the polyuronic acids did not split off carbon dioxide. The determination of the reducing substances in solution showed that

¹) Extraction of hemicellulose from the initial materials by immediate treatment with 12% HCl was also tried but it gave a negative result, increasing the yield of lignin; wood 26.26, grass 12.38, moss 24.06%.

²) Later study of the lignin residue showed that a large part of it was transformed into a state soluble in alkali.

³) The methylation was carried out in a stream of nitrogen as proposed, quite correctly, by Dragunov, Zhelakhovtseva and Strelkova [4].

TABLE 1

Analytic data on three types of plant

Name of component parts	Analytic data (in % of organic part of the plant materials)		
	Wood	Grass	Moss
Hydrolyzed by 1 N HCl	19.41	35.25	50.93
Substance hydrolyzed by concentrated sulfuric acid and reckoned as cellulose.....	40.62	23.25	15.12
Unhydrolyzed residue (lignin).....	25.48	20.95	17.82
Reducing substance reckoned as glucose.....	18.77	29.61	32.88
Pentosans ¹	9.63	24.48	15.20
Uronic acids ²	2.99	7.03	11.80

TABLE 2

Results of analysis of the residue from hydrolysis with 1 N HCl

Name of component parts	Analytic data (in % of organic part of the plant materials)		
	Wood	Grass	Moss
Substance hydrolyzed by 12% HCl.....	34.72	15.13	12.89
Substance hydrolyzed by concentrated sulfuric acid and reckoned as cellulose.....	6.53	8.30	2.50
Unhydrolyzed residue (lignin).....	24.86	16.56	13.49
Reducing substance reckoned as glucose.....	3.58	12.35	3.29
Pentosans.....	2.88	1.03	2.17
Uronic acids.....	2.76	6.12	8.26

TABLE 3

Comparative figures for two preparations of grass lignin

Method of hydrolysis of hemicellulose	Methoxyl group content (% of the organic part of the lignin)			
	Initial methoxyl	Total methoxyl	Methoxyl hydroxyls	Methoxyl carboxyls
Without acid.....	11.92	32.43	30.16	2.27
With 12% acid.....	15.66	20.73	20.73	None

the polyuronic acids were also not hydrolyzed by concentrated acids, because they could not be got into solutions; the content of uronic acids in the initial materials was 19.69%, and the hydrolyzable cellulose was 79.73%. The non-hydrolyzed residue (20.27%) agrees almost quantitatively with the uronic acids.

By analogy with these data it might be expected that in the natural plant substance the polyuronic acids, if not all then at least in large part could not

¹) The pentosans here and further on are shown calculated as uronic acids [3].

²) The uronic acids were determined in the initial materials by the method of Tollens and Lefevre.

TABLE 4

Content of pentosans and uronic acids in lignin residues

Name of component part	Content (in % of the organic part of the plant materials)		
	Wood	Grass	Moss
Pentosans.....	0.90	None	0.37
Uronic acids.....	0.99	2.07	2.49

be hydrolyzed by concentrated sulfuric acid and consequently that the acid method of analysis would lead to an error that could not be overlooked. We restrain ourselves from a final judgment of the behavior of pentosans since we can only adduce the determination of cellulose in grass by the method of Kurshner and Hoffer [3] giving its quantity, including that of any impurity, as 23.96%, and the general quantity of substance hydrolyzed by sulfuric acid as 22.25%. These data indicate that pentosans together with cellulose are not hydrolyzed but, like uronic acid, go into the lignin residue.

While this explanation of the role of difficultly hydrolyzable hemicellulose does enable the accuracy of analysis of plant substances to be increased to some extent, this cannot be done by hydrolysis with dilute acid. Examination of the data in Table 1 already shows that the quantity hydrolyzed by 1.0 N HCl agrees with the figure for reducing substance only in the case of pinewood, while in the grass and particularly in the moss the differences were 5.64 and 18.5% respectively. This was without doubt known earlier, but conclusions have not been drawn from it so far. We suggest that it may be attributed to two causes: 1) together with carbohydrates, non-reducing products are also present in solution; and 2) on hydrolysis the carbohydrates partially lose their reducing power and are therefore missed.

We think that the second cause gives the larger effect because it is difficult to suppose that in the moss, for example, there is up to 18% of an unobserved compound of another class. Independently we found other bodies present, e.g., nitrogenous and tanning substances, a large part of which could be extracted with water, for example 10.76% in the moss. Hence they can hardly comprise a fifth of the whole organic mass of the plants.

If the carbohydrate complex, by changing its character, can transform into soluble products, this, to our way of thinking does not exclude the possibility of converting it to an insoluble substance. To elucidate this matter we resorted, as described above, to exhaustive methylation of the grass treated with organic solvents and water, i.e., containing practically all the carbohydrate complex and lignin. Afterwards the product was subjected to successive hydrolysis by 1 N HCl and concentrated sulfuric acid. The methylated lignin thus separated was compared with lignin obtained by the stepwise hydrolysis of the original material, but methylated after separation. If the carbohydrate complex did not participate in the formation of the lignin residue then both preparations should be the same.

This method was used earlier by Vener in working on lignins of certain woods with the main difference that the products were subjected to methylation after repeated treatment with dilute acids, i.e., when freed from the main bulk of the hemicellulose [5]. The preparations thus obtained corresponded completely in their total methoxyl content, for example: in pine 25.05 and

25.25%; in birch 28.08 and 28.08%; in lime 29.19 and 29.73%. From these data it can, however, only be concluded that the products of hydrolysis of cellulose under the experimental conditions were not converted to a lignin residue, but nothing can be said about the importance of hemicellulose. The sample of grass subjected in our experiments to methylation and subsequent hydrolysis contained (in % of its organic part): C-68.56, H-5.91 and total methoxyl 22.05¹. But the analysis of this same lignin methylated after its separation gave (in %) C 67.16, H 6.60 and total methoxyl 32.43. The first preparation showed from the figure for its reactive groups a closer similarity to the lignin which was obtained after complete removal of the hemicellulose than to ordinary lignin (Table 3).

Thus where the hydroxyl group was converted to methoxyl it can be asserted that the condensation of the carbohydrate complex is strongly inhibited while when the carboxyl and hydroxyl groups are free this does not happen; consequently, the analytic data confirms the partial conversion of the carbohydrate, in hydrolysis by dilute acid, into a lignin residue, thus raising the yield of the latter. This throws doubt on all determinations of lignin in plant substances carried out by one or other of the acid methods and requires the selection of an entirely different method of separating the carbohydrate complex, particularly uronic acids and pentosans, from lignin. We noted above a method of extraction with alkali solution. We tested this only on one sample, the grass.

The grass, preliminarily treated with benzene, ethylalcohol and water, was heated for eight hours on a boiling water bath with 0.5 N solution of caustic soda in a stream of nitrogen. The residue was filtered off and, after washing with water and roughly drying, it was subjected again to treatment with alkali.

Altogether 40.16% went into solution and 43.85% did not dissolve, percentages based on the organic part of the grass. 14.90% of cellulose was found in this residue along with 4.35% lignin containing 18.79% methoxyl group. After concentrating the alkali solution in a stream of nitrogen, acidifying it with hydrochloric acid, and heating, a residue separated out which was afterwards purified by dissolving it again in alkali, precipitating it, and washing it with water. Its yield was 9.54% of the organic part of the original material and its elementary composition was C 62.35, H 5.43%. Methoxyl was entirely absent.

The latter circumstance does not permit this deposit to be considered as grass lignin, which contains 11.92% methoxyl, the more so as it was thrown down only as a result of heating the acidified solution, in other words after hydrolysis of the hemicellulose. Apparently it was also the product of the carbohydrate complexes which are formed in the acid method of separating lignin of some plants as its main component part.

SUMMARY

1) Hydrolysis of plant substances by 1 N HCl did not extract from them either all the pentosans or all the uronic acids.

2) The lignin residues separated by concentrated mineral acids, likewise still contained undecomposed pentosans and uronic acids, the presence of which may be explained by the existence in the lignin molecule of one or even several carboxyl groups.

¹) The possibility of saponification of esters in the presence of sulfuric acid was taken into consideration, and the preparation obtained was again methylated with methanol after hydrolysis, wherein saponification was not observed.

3) It has been shown that about 80% of the polyuronide complex, as exemplified by that obtained by the oxidation of cellulose, is not decomposed by concentrated sulfuric acid under the conditions where lignin is separated with elimination of CO₂.

4) By methylating lignin before and after separating it from plant substances it was shown that hemicellulose takes part in the formation of the lignin residue during its hydrolysis by 1 N HCl.

5) The isolation of the lignin by extracting it with alkali is also connected with the acid hydrolysis of the carbohydrate complex, which throws doubt on the natural character of the product separated.

6) It has been shown that 0.5 N caustic soda extracts from the grass (Eriophorum Vaginaturn) a product which is closer in elementary composition to lignin but is completely deficient in methoxyl; a large part of it remains insoluble in alkali.

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BRIEF COMMUNICATIONS

VISCOSITY OF HALOGENS AND OF SOME HALIDES

D. A. Pospekhov

In previous papers [1,2] we have examined the dependence of viscosity on temperature (in the liquid state) for organic compounds belonging to a homologous series. It was shown that for substances belonging to seven homologous series the log of the viscosity was directly proportional to the reciprocal of the absolute temperature, which indicates that the relationship is exponential. Extrapolation on the high temperature side showed that the lines relating to members of one and the same series practically intersected at the same point, the position of which was characteristic for the given homologous series. The indicated correlation could not be applied to the first one or two members of the series.

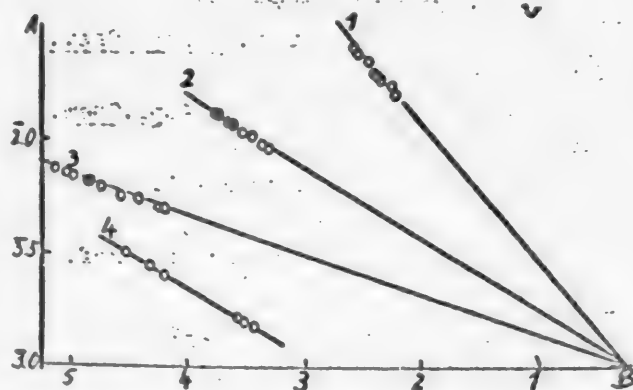


Fig. 1. Dependence of the log of the viscosity on the reciprocal absolute temperature for liquid chlorine, bromine, iodine, and ammonia. A = $\log \eta$; B = $1000/T$. 1 = Iodine; 2 = bromine; 3 = chlorine [4]; 4 = ammonia [5].

It seemed interesting to examine the existence of such a correlation among inorganic substances.

As can be seen from Figure 1 the correlation described is observed in liquid chlorine, bromine and iodine. The value of $\log \eta$ is plotted on the ordinate, η = viscosity in poises; the value of $1000/T$ is plotted on the abscissa where T = absolute temperature. The point of intersection of the exponent obtained by extrapolation occurs at about $1000/T = 0.23$ which corresponds to 4070° . As in the case of the homologous series of organic compounds, this point cannot be given a direct physical meaning because it lies higher than the critical

temperature of the least volatile halogeniodine (critical temperature 553° [3]). Generally the position of such points characterizes the interconnections of the temperature co-efficients of viscosity of the corresponding substances.

We have not found data in the literature about the viscosity of liquid fluorine, hence we cannot decide how the plot of $\log \eta$ vs $1/T$ for this substance lies on the graph.

On Figure 1 also the graph of $\log \eta$ vs $1/T$ for ammonia has been drawn for comparison; as can be seen, the exponent for ammonia quite clearly deviates from those for the halogen.

Let us examine further the dependence between these parameters for silver-chloride, -bromide and -iodide (Figure 2). As can be seen the picture here is different from that with the liquid halogens. The plot for silver iodide is curvilinear; the dependence for silver chloride and bromide is linear. Thus there is no basis for speaking of a correlation characteristic of the viscosities

of members of one and the same homologous series.

What has been said may be put in this way. Insofar as the data presented by us in the previous papers [1,2] indicates the existence of a characteristic homologous series for viscosities then the series chlorine, bromine and iodine can be considered as a homologous series. On the other hand the series silver-chloride, -bromide and -iodide on the same basis cannot be considered as a true homologous series. The limited quantity of information about the viscosity of inorganic substances in the liquid state which is to be found in literature makes it impossible to examine this question in more detail.

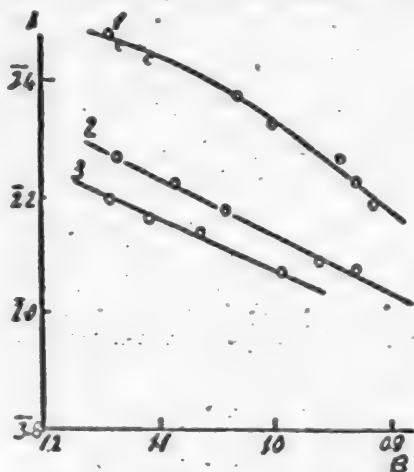


Fig.2. Dependence of the log of the viscosity on the inverse absolute temperature for silver, chloride, bromide and iodide.

A = $\log \eta$; B = $1000/T$. 1 = Silver iodide; 2 = silver bromide; 3 = silver chloride [6].

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¹⁾ See Consultants Bureau English translation, p. 175.

²⁾ See Consultants Bureau English translation, p. 297.

EFFECT OF TEMPERATURE ON THE PROCESS OF ION EXCHANGE ON SYNTHETIC CATIONITES

E. S. Peremyslova and R. P. Stashko

In the literature there is hardly any specialized work devoted to the study of the effect of temperature on ion exchange. Some information about the increase of the exchange capacity of synthetic resins at raised temperatures is given by Smirnov [1] (sulfophenolic resin of the type Vofatite P and Cationite PFSK); Streicher, Pearson and Bowers [2] came to the same conclusions and explained this by the fact that at raised temperatures the viscosity of water is reduced and its ability to penetrate into the pores of the ionites increases. However it is not known from these papers how the exchange capacity of the ionites, total or 'apparent', increases with increase of temperature; if an increase of temperature exerts its effect by changing the rate of diffusion of ions from the solution into the cationite this should be referred to as a raising of the 'apparent' exchange capacity, while if temperature also causes a change in the degree of dissociation this would entail a change of the total exchange capacity. To elucidate this we carried out experiments in which the effect of temperature on the 'apparent' exchange capacity of cationites was determined by dynamic methods.

0.01 N solutions of CaCl_2 and KCl were passed through a layer of hydrogen cationite (20g), placed in a tubular glass filter, at 3m/hour at constant temperature. The acidity of the filtrate was determined and the "apparent" exchange capacity was calculated from the data obtained.

Experiments were carried out at temperatures of 2, 15 and 75°. A sulfophenolic resin of the Vofatite P type with the active sulfo groups located mainly in the side chains, and a parapheniosulfonic acid cationite (PFSK) with the active sulfo groups mainly in the nucleus, were examined. The results of the experiment are set forth in Table 1.

TABLE 1

Effect of temperature on ion exchange under dynamic conditions

Temperature (°C)	Cationite	" Apparent" exchange capacity (in mg-ec/g)		Ratio of exchange capacity of cationites
		Ca^{2+}	K^+	
2	Vofatite P	0.92	0.78	1.18
	Cationite PFSK	1.57	1.30	1.20
15	Vofatite P	0.95	0.80	1.19
	Cationite PFSK	1.60	1.34	1.19
75	Vofatite P	1.05	0.90	1.17
	Cationite PFSK	1.70	1.44	1.18

The data set out indicates that the "apparent" exchange capacity of ionites depends on the temperature, increasing proportionately to it. Apart from this it follows from Table 1 that the ratio of the exchange capacities of cationites for Ca^{2+} and K^+ remain constant at any temperature in the temperature region investigated. This means that the character of the change of exchange capacities of cationites is identical with respect both to Ca^{2+} and K^+ .

To explain this change of the "apparent" exchange capacity, experiments under static conditions were carried out to elucidate the effect of temperature on the rate of ion exchange.

1 g of the hydrogen cationite was kept in contact with 500ml of 0.01 N solutions of CaCl_2 and NaCl at constant temperature. After a definite interval of time the acidity of the filtrate was determined, on the basis of which the exchange capacity of the cationite was calculated.

The experiments were performed at 15 and 75°. The ionite employed was a resorcylic cationite with active carboxyl group, and the cationite PSFK.

The results of experiments are set forth in Table 2., from which it follows that temperature has an effect of the kinetics of the ion exchange processes; raising it promotes the more rapid attainment of equilibrium. This is explained by an increase of the rate of diffusion of ions from the solution into the cationite when the temperature is raised. The effect of temperature is particularly marked on the weakly acid cationites (resorcylic cationite).

TABLE 2

Effect of temperature on the rate of ion exchange under static conditions									
Time of contact of cationite with solution	Exchange capacity (in mg.eq./l)				Time of contact of cationite with solution	Exchange capacity (in mg.eq./l)			
	Ca ²⁺		Na ⁺			Ca ²⁺		Na ⁺	
	15°C	75°C	15°C	75°C		15°C	75°C	15°C	75°C
Resorcylic cationite					Cationite PSFK				
10 minutes	0.057	0.085	0.085	0.114	10 minutes	0.40	0.70	0.70	0.70
30 "	0.057	0.114	0.114	0.142	30 "	0.68	1.06	0.94	0.80
1 hour	0.057	0.114	0.114	0.171	1 hour	0.88	1.10	1.00	1.00
2 hours	0.085	0.171	0.142	0.171	2 hours	1.25	1.25	1.10	1.10
3 hours	0.114	0.228	0.142	0.171	3 hours	1.40	1.40	1.10	1.10
4 hours	0.114	0.257	0.142	0.171	4 hours	1.40	1.40	1.10	1.10
5 hours	0.114	0.285	0.171	0.171	5 hours	1.40	1.40	1.10	1.10
6 hours	0.142	0.313	0.171	0.171	6 hours	1.40	1.40	1.10	1.10
1 day	0.142	0.313	0.171	0.171	1 day	1.40	1.40	1.10	1.10

TABLE 3

Effect of temperature on ion exchange under static conditions.						
Name of cationite	Equilibrium exchange capacity (in mg.eq./liter)					
	Ca^{2+}			Na^+		
	2° C	15° C	75° C	2° C	15° C	75° C
Resorcylic	0.09	0.12	0.3	0.12	0.12	0.12
Vofatite P	0.99	0.99	0.99	0.72	0.72	0.72
PSFK	1.4	1.4	1.4	1.1	1.1	1.1

Experiments were also carried to elucidate the effect of temperature on the equilibrium exchange capacity of cationites. They were made with 1 g of hydrogen-cationite in 0.01 N solutions of CaCl_2 and NaCl at temperatures of 2, 15 and 75°. The results are in Table 3.

The data of Table 3 indicates that the equilibrium exchange capacities for such cationites as Vofatite P and Cationite PSFK, i.e. cationites having fairly

strong acid properties, does not depend on temperature.

The equilibrium exchange capacity with respect to Na^+ of resorcylic cationite, which is weakly acid likewise does not depend on temperature. For Ca^{2+} such a dependence is found and increases the equilibrium exchange capacity of cationite proportional to the rise of temperature.

This may be explained by an increase in the diameter in the micropores of the resorcylic cationite at elevated temperatures and consequently by an increase of the number of micropores available for penetration by the ions of calcium. For the Na^+ ions temperature is not important, since it has a radius of 0.98 Å i.e., less than that of the Ca^{2+} ion (1.06 Å) and therefore all the micropores of the cationite are accessible to the Na^+ ions at all temperatures.

An exactly similar explanation can be advanced for the fact that at temperatures lower than 15°, the equilibrium exchange capacity for Ca is less than that for Na^+ i.e. Ca^{2+} and Na^+ change places in the exchange order. Evidently the exchange capacity for Ca^{2+} , decreasing with decrease of temperature becomes lower than the exchange capacity for Na^+ which does not depend on temperature.

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METHOD FOR CALCULATING MATERIAL BALANCES OF CYCLIC PROCESSES¹

D.A. Epshtein.

Simple two-way irreversible reactions are as a rule carried out in industry in a cyclic manner [1]. The calculation of the material balance for a circulating process requires the use of a special method, which is described here with reference to the synthesis of ammonia.

The flow sheet for the process is shown in Fig. 1, and a diagram of the material balance in Fig. 2. The method of calculation applies to the circulating process and also to the other scheme. The calculation is carried out for one mol of product in molar units. All material flows are taken into account (cf. (2)).



Fig. 1. Flow sheet for the synthesis of ammonia. 1 - High pressure compressor; 2 - pump; 3 - oil separator; 4 - filter; 5 - converter; 6 - water cooler; 7 - separator; 8 - circulation of gas; 9 - ammonia; 10 - water; 11 - fresh gas.

Fresh nitrogen-hydrogen mixture of stoichiometric composition, containing known quantities of inert gases (argon, methane, etc) is mixed with the circulating gas. The latter contains a definite quantity of inert gases, ammonia, and a stoichiometric mixture of nitrogen and hydrogen. The gas mixture enters the converter in which ammonia is synthesized and passes out of it into the water cooler and separator. Here ammonia is separated together with gases soluble in it: nitrogen, hydrogen, argon, methane. A portion of the gas mixture leaving the separator is returned to the system in order to maintain a constant concentration of inert gases in the cycle; the main quantity is returned by the circulating pump to the converter.

We use the following symbols: N = mols of mixture or of mixture component; γ = mole fraction of component in mixture; n = solubility of gas in liquid ammonia in moles/mole. The symbols for denoting gas mixtures and substances are; m = stoichiometric mixture of hydrogen and nitrogen ($3H_2 + N_2$); i = inert gases (A , CH_4 , etc); a = ammonia. The gas streams are numbered as shown in Fig. 2.

For denoting the number of moles and the mole fractions of any substance in a corresponding gas mixture we use the following index system: the upper index indicates the substance, the lower index the number of the gas stream. For example; N_2^a = number of moles of ammonia in the circulating gas, γ_1^m mol fraction of the stoichiometric mixture of hydrogen and nitrogen in a fresh gas and so on.

The initial data for the calculation are the following;

(a) Composition of the fresh gas; γ_1^A , $\gamma_1^{CH_4}$; remainder (γ_1^m) = stoichiometric mixture of nitrogen and hydrogen;

(b) Composition of circulating gas: γ_2^A , $\gamma_2^{CH_4}$, γ_2^a ; remainder (γ_2^m) = stoichiometric mixture of nitrogen and hydrogen;

¹ Communication III of a series on "Scientific Basis for the Design of Chemical - Technological Processes."

of ammonia, to which figure also must be added the loss with the product gases; 2) by solution in liquid ammonia; and 3) by loss in the product gases. Hence the following equation for the nitrogen-hydrogen mixture:

$$N_1 Y_1^m = 2 + n^m + N_3 (Y_2^m = 2 Y_2^a). \quad (3)$$

where 2 = number of moles of mixture required for reaction to produce one mole of ammonia; $N_3 2Y_2^a$ = number of moles of mixture consumed in the formation of ammonia lost with the product gases. If the solubility of nitrogen and hydrogen differs considerably under the conditions given then n^m changes to the sum $n^{H_2} + n^{N_2}$.

The ammonia balance in the converter has the form:

$$N_2 Y_2^a + 1 + N_3 Y_2^a = N_4 Y_4^a. \quad (4)$$

Solving Equations (2) and (3) we find that N_3 the number of moles of gas produced is:

$$N_3 = \frac{(2 + n^m) Y_1^i - n^i Y_1^m}{Y_1^m Y_2^i - Y_1^i (Y_2^m + 2Y_2^a)}. \quad (5)$$

knowing N_3 , we determine the quantity of fresh gas N_1 from Equation (2)

$$N_1 = \frac{2 + n^m}{Y_1^m} + N_3 \frac{Y_2^m + 2Y_2^a}{Y_1^m}. \quad (6)$$

The quantity of circulating gas N_2 is calculated from Equation (4) and (1):

$$N_2 = \frac{(1 + N_3 Y_2^a) (1 + Y_4^a) - N_1 Y_4^a}{Y_4^a - Y_2^a}. \quad (7)$$

The data obtained are sufficient for setting up balances in all cyclic apparatus and for the determination of the composition of all gas streams.

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ELECTROLYSIS OF ZINC SALTS¹

M.T.Kozlovsky P.P Tsyb and E.I.Ruzina

S.M.Kirov Kazakh State University

A considerable number of investigators have studied the electrolytic deposition of zinc at a mercury cathode and have studied the properties of its amalgams [1-4]. However, in this research on the electrolysis of zinc salts, the effect of different factors on the cathode and anode potentials has not been studied in detail. Our work is an extension of our investigation of electrolysis with a mercury electrode and has been devoted to an elucidation of the effect, on the cathode potential in the deposition of zinc and on the anode potential in the decomposition of amalgams, of the same factors, whose effect was studied in the previous investigations.

The set-up for carrying out the experiments was described in our first communication, so that here we limit ourselves only to a short record of the experimental data.

EXPERIMENTAL

The zinc sulfate which was used for carrying out the experiment was examined spectrographically and shown to contain only very small quantities of lead, copper, iron, manganese and calcium, below the limits of chemical determination. Zinc was determined in solution with potassium iodate after precipitating its mercurithiocyanate salt [5]. Experiments on the complete preparation of zinc from the electrolyte in electrolysis were made after reaction with potassium ferrocyanide [6].

Initially experiments were carried out to elucidate the dependence, of the cathode potential in the electrolytic deposition of zinc and of the anode potential in the electrolytic decomposition of the amalgam obtained, on the concentration of zinc in the amalgam at different current densities and different temperatures. For this purpose a solution of zinc sulfate of known concentration was electrolyzed and in this way amalgams containing 0.1, 1, 2, 4, 8 and 12 g-atoms of zinc per liter were obtained; then measurements of the cathode potential were made and, after reversing the current the anode potential was measured. The electrolyte for these measurements was a solution of zinc sulfate containing 0.1 g.ion of zinc per liter and g-equiv. of sulfuric acid. The experimental data are given in Table 1.

It emerges from the data in Table 1 that, as the concentration of zinc in the amalgam increases, both the cathode and anode potentials become more negative so that at zero c.d. the potential difference between an amalgam containing 0.1 and one containing 12 g.atom of zinc per liter of mercury was 0.05 - 0.06 V, i.e., approaches the theoretical value calculated from the Nernst formula for amalgam cells:

$$E_2 = E_1 + \frac{RT}{nF} \ln \frac{c_1}{c_2} = E_1 + 0.029 \log \frac{0.1}{12} = E_1 - 0.06$$

It should be noted that, when the concentration of zinc in the amalgam is high, (12 g-atom per liter of H₂) it became more viscous, thus reducing the

¹) Communication III of a series dealing with the investigation of electrode potentials in the electrolysis of salts of different metals with a mercury electrode

Dependence of the Cathode and Anode Potentials on the Concentration or Zinc in the Amalgam. (3-atoms/liter)*

Zinc in the Amalgam (0.5-atm./liter)*																
Concentration of zinc in electrolyte in g.-atoms/liter	Temperature (deg.)															
	18-23					48-53					78-83					
	Current density (A/cm ² · 10 ⁻³)															
	0	2.2	11	22	44	65	87	110	0	2.2	11	22	44	65	87	110
Cathode																
0.1	0.77	0.81	0.85	0.90	0.97	1.06	1.12	1.16	0.76	0.79	0.82	0.85	0.92	0.98	1.06	1.11
1	0.79	0.83	0.86	0.91	1.0	1.07	1.12	1.17	0.78	0.80	0.82	0.87	0.94	1.0	1.06	1.11
2	0.83	0.87	0.89	0.94	0.99	1.04	1.11	1.15	0.80	0.82	0.84	0.88	0.95	1.02	1.08	1.13
4	0.81	0.84	0.86	0.90	0.96	1.06	1.12	1.17	0.79	0.82	0.85	0.89	0.96	1.03	1.08	1.12
8	0.81	0.84	0.87	0.93	1.0	1.06	1.12	1.17	0.80	0.83	0.85	0.89	0.96	1.02	1.07	1.12
12	0.83	0.85	0.87	0.94	1.03	1.11	1.18	1.23	0.81	0.83	0.87	0.91	0.98	1.07	1.13	1.19
Anode.																
0.1	0.76	0.75	0.72	0.67	0.58	0.49	0.41	-	0.75	0.72	0.69	0.64	0.56	0.42	0.41	-
1	0.81	0.78	0.74	0.70	0.61	0.54	0.48	-	0.77	0.76	0.74	0.70	0.63	0.55	0.51	-
2	0.80	0.78	0.75	0.71	0.62	0.55	0.50	-	0.80	0.78	0.76	0.72	0.65	0.59	0.51	-
4	0.82	0.80	0.76	0.72	0.65	0.59	0.53	-	0.79	0.77	0.75	0.69	0.63	0.59	0.52	-
8	0.83	0.80	0.78	0.72	0.66	0.59	0.53	-	0.80	0.79	0.77	0.72	0.66	0.60	0.53	-

TABLE 2
Effect of Concentration of Zinc in the Electrolyte on the Cathode and Anode Potentials

Concentration of zinc in electrolyte in g.-atoms/liter	Temperature (deg.)																								
	18-23					48-53																			
	Current density (A/cm ² · 10 ⁻³)																								
Cathode																									
	0	2.2	11	22	44	65	87	110	0	2.2	11	22	44	65	87	110									
0.01	0.84	0.85	0.87	0.90	0.97	1.06	1.12	1.16	0.76	0.79	0.82	0.83	0.92	1.02	1.10	1.17	1.24	0.80	0.82	0.84	0.87	0.97	1.06	1.15	1.19
0.05	0.81	0.82	0.84	0.89	0.94	1.03	1.10	1.13	0.77	0.80	0.83	0.85	0.93	1.0	1.10	1.15	1.18	0.77	0.79	0.81	0.85	0.92	1.0	1.02	1.07
0.1	0.81	0.83	0.85	0.92	0.99	1.08	1.13	1.16	0.79	0.80	0.83	0.86	0.96	1.05	1.10	1.15	1.15	0.76	0.77	0.80	0.84	0.93	1.0	1.07	1.14
0.5	0.79	0.80	0.83	0.89	0.96	1.01	1.10	1.13	0.78	0.79	0.81	0.87	0.92	1.0	1.09	1.12	1.12	0.75	0.76	0.78	0.80	0.87	0.93	1.01	1.08
Anode																									
	0	2.2	11	22	44	65	87	110	0	2.2	11	22	44	65	87	110									
0.01	0.84	0.83	0.82	0.76	0.69	0.61	0.54	0.49	0.81	0.79	0.76	0.72	0.66	0.57	0.52	0.47	0.80	0.79	0.76	0.73	0.67	0.59	0.5	0.46	
0.05	0.83	0.80	0.77	0.73	0.66	0.60	0.53	0.48	0.80	0.79	0.77	0.72	0.64	0.57	0.51	0.47	0.79	0.77	0.75	0.71	0.64	0.56	0.50	0.46	
0.1	0.81	0.80	0.77	0.72	0.65	0.58	0.53	0.47	0.79	0.78	0.75	0.71	0.65	0.58	0.52	0.46	0.77	0.75	0.73	0.70	0.63	0.56	0.51	0.45	
0.5	0.80	0.79	0.76	0.72	0.66	0.60	0.53	0.47	0.78	0.76	0.74	0.71	0.65	0.57	0.50	0.46	0.75	0.74	0.72	0.70	0.66	0.57	0.50	0.45	

this and subsequent tables

*In this and subsequent tables the potentials are negative with respect to the normal hydrogen electrode.

surface of the mercury electrode (amalgam stirred), and this in its turn caused an increase in the true current density. At lower temperatures and higher current densities a large negative displacement of the potentials was observed. At a temperature of 78 - 83°, i.e., when the amalgams became less viscous, this phenomenon did not take place. Furthermore, when the anode was polarized, the potential differences between amalgams containing 0.1 - (8 g-atom) of mercury increased with increase in current density and likewise with rise of temperature, which is explained, on the one hand, by an increase of the concentration polarization at high current densities, and, on the other hand, by a direct solution of zinc in the sulfuric acid (local cells whose work is not recorded on the ammeter), which increases at high temperatures.

As the temperature rises, the concentration polarization decreases and so does the hydrogen overvoltage. These factors promote a displacement of the potential towards the positive side, which is observed in our experiments (Table 1). A large positive potential displacement at high current densities is connected, as already noted, with a change of the true surface of the mercury electrode.

As the temperature rises, the rate of diffusion of zinc dissolved in the mercury increases, because the concentration of the atoms of zinc in the surface layer of the mercury anode increases; the potential of the anode should become more negative. However, it appears from the experimental data that with rising temperature the anode potential becomes more positive. The cause of this may be sought, as mentioned already, in a direct solution of zinc in sulfuric acid.

The dependence of the cathode and anode potentials on the current density is shown in Table 1. With increase in c.d. the concentration polarization increases both for cathode and anode processes, which displaces the cathode potential towards the negative and the anode potential towards the positive.

The next experiments were carried out to elucidate the dependence of the cathode and anode potentials on the concentration of zinc in the electrolyte. Amalgams containing 1 g-atom zinc per liter of mercury were obtained by electrolysis of solutions of zinc sulfate of known concentrations, and measurements of the cathode potential and (after reversing the polarity), of the anode potential, were made. The potential measurements were made in electrolytes containing 0.01, 0.05, 0.1 and 0.5 g-ion of zinc per liter and also containing 1 g-equiv. of sulfuric acid. The data are in Table 2.

It follows from these data that as the concentration of zinc in the electrolyte increases both the cathode and the anode potentials become more positive in agreement with the Nernst formula. However, at a low concentration of zinc (0.01 g-ion per liter) a large change of potential of the cathode was observed when the c.d. increased, which is due to concentration polarization.

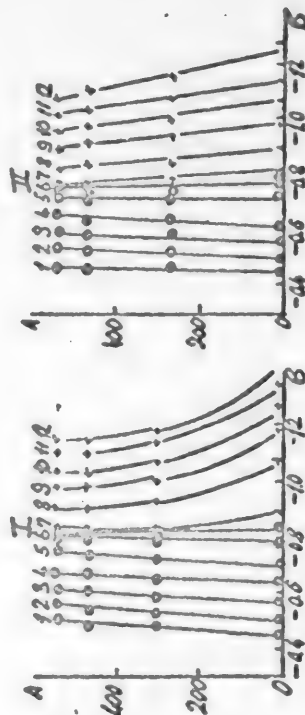
Further, a series of experiments were carried out to elucidate the effect of the rate of stirring on the cathode and anode potentials. For this purpose amalgams were obtained containing 1 g-atom of zinc per liter of mercury, and measurements of potentials were carried out at 300, 460 and 540 r.p.m. The electrolyte was a solution of zinc sulfate containing 0.1 g-ion of zinc and 1 g-equiv. of sulfuric acid per liter. The experimental data are shown in the figure.

From the course of the curves showing the cathode and anode potentials as a function of the rate of stirring, it is clear that as the rate of stirring increases the cathode potential becomes more positive, and the anode potential more negative. This is explained by the fact that, on the one hand, as the rate

TABLE 3

Experimental data on the decomposition of zinc on a mercury cathode

Initial concentration of Zn in electrolyte (g/200 ml)	o.d. ($A/cm^2 \cdot 10^{-3}$)	Mean p.d. across cell terminals (in V)	Temp. (deg)	Variation of cathode potential (V) with time (in minutes)												Current efficiency (%)	
				0	5	10	15	20	25	30	35	40	45	50	55		
0.65	0.05	11.5	20	1.05	1.10	1.12	1.13	1.13	1.13	1.13	1.25	1.28	1.28	1.23	-	-	38
0.65	0.05	11.3	50	1.01	1.01	1.05	1.11	1.15	1.18	1.20	1.20	1.20	1.20	1.20	-	-	43
0.65	0.05	13.5	20	1.24	1.27	1.29	1.39	1.50	1.50	1.50	1.50	-	-	-	-	-	32
0.65	0.05	13.0	50	1.18	1.23	1.30	1.42	1.46	1.46	1.46	1.46	-	-	-	-	-	32
1.3	0.1	11.5	20	1.03	1.08	1.09	1.09	1.10	1.12	1.14	1.18	1.18	1.24	1.26	1.26	1.26	57
1.3	0.1	11.3	50	1.0	1.0	1.03	1.04	1.04	1.05	1.05	1.14	1.14	1.18	1.20	1.20	1.20	57
1.3	0.1	13.5	20	1.20	1.25	1.36	1.44	1.44	1.47	1.47	1.47	1.47	1.47	-	-	-	51
1.3	0.1	13.0	50	1.16	1.18	1.19	1.23	1.38	1.49	1.49	1.49	1.49	1.49	-	-	-	51



Dependence of the cathode and anode potentials on the rate of stirring. A - R.p.m. of stirrer; B - anode and cathode potentials (V). Anode o.d. ($in A/cm^2$): 1 - 0.11; 2 - 0.087; 3 - 0.064; 4 - 0.044; 5 - 0.022; 6 - 0.0022. Cathode c.d. ($in A/cm^2$): 7 - 0.022; 8 - 0.022; 9 - 0.044; 10 - 0.065; 11 - 0.087; 12 - 0.11. I - Temperature 18-23 deg C; II - Temperature 78-83 deg C.

* In the calculation of the current efficiency the duration of the electrolysis was taken as the time elapsing until the cathode potential was sufficiently constant.

of stirring increases the concentration polarization is decreased due to an equalization both of the concentration of ions in the electrolyte (close to the electrode) and of the concentration of metal in the amalgam and, on the other hand, as the rate of stirring increases, there is a certain increase of the surface of the mercury electrode, which causes a lowering of the real c.d. This increase should also somewhat lower the hydrogen overvoltage.

Finally, experiments were carried out on the electrolytic deposition of zinc on the mercury cathode, and the amalgam obtained was decomposed electrolytically. For this purpose, 200 ml of a solution of zinc sulfate of known concentration were placed in a cell, the electrolyte being 1 N in H_2SO_4 . Electrolysis was carried on until the zinc had been completely extracted from the solution, after which the polarity was reversed, the amalgam being made the anode and the platinum gauze the cathode, and the electrolysis was carried on until all the zinc had been extracted from the amalgam. In the decomposition of the amalgam the anode potential shifted only slightly towards the positive, and only when the zinc had practically completely transferred from the amalgam to the electrolyte, was there a sharp rise in the anode potential to values necessary for the oxidation of mercury. At the same time turbidity appeared in the electrolyte as a result of the transfer into the solution of ions of univalent mercury, whereby mercurous sulfate was formed with the sulfate ions. At this point the electrolysis was stopped, and the zinc in solution quantitatively determined. In this way it was established that the yield of zinc was 99-99.7%, i.e., in the electrolytic decomposition of the amalgam the zinc is practically completely extracted into the electrolyte. The experimental data on the electrolytic deposition of zinc on a mercury electrode are contained in Table 3.

From the experimental data in this table, it is seen that the deposition of zinc under the conditions quoted occurs at a current efficiency of 32-57%. The low efficiency is due to the simultaneous discharge of hydrogen and zinc ions.

SUMMARY

1) Measurements have been made to establish the dependence, of the cathode potential in the electrolytic deposition of zinc on a mercury electrode and of the anode potential in the electrolytic decomposition of the amalgams obtained, at different c.d.'s and temperatures: a) on the concentration of zinc in the amalgam; b) on the concentration of zinc ions in the electrolyte; and c) on the rate of stirring.

2) It has been established that in the electrolytic decomposition of its amalgams zinc can be almost completely extracted into the electrolyte.

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STUDY OF THE RATE OF FORMATION OF SUGAR HUMIN SUBSTANCES

V. A. Sainov

Leningrad Technological Institute for the Food Industry

If monosaccharides are acted upon by concentrated acids at room temperatures, or by hot dilute acids along with other products, compounds are formed which are dark in color, insoluble in water, and which are called sugar humin substances.

From the literature [1] it is known that the humin substances form more quickly with concentrated sulfuric acid than with concentrated hydrochloric acid. The reaction is speeded up by raising the temperature. Hahn [2] studied the development of humin substances in dilute sulfuric acid at 100°. From his investigations it appears that the production of humin from galactose is somewhat slower and from fructose on the other hand considerably quicker than from glucose. If a monosaccharide is heated in water to 100° and higher, then the huminification proceeds at some speed or other even without addition of acid, at the expense of the organic acids which appear as a result of the breakdown of the sugar [3].

Thus the data at our disposal is more qualitative than quantitative. The objective of our work was to investigate the rate of formation of the sugar humin substance.

EXPERIMENTAL

Method of investigation. The huminification of monosaccharides by concentrated acids was carried out uniformly as follows.

In several 50 ml flasks 0.5 g of anhydrous monosaccharides were placed, and to each 10 ml of acid was added. After careful shaking, the flasks were closed by glass stoppers and kept in a thermostat for a definite time. Afterwards their contents were transferred quantitatively to measuring cylinders, diluted to 15 times their volume and allowed to stand for 24 hours. The solutions were then filtered through a hard paper filter; the precipitates on the filter were washed with distilled water and dried to constant weight at 110°. The weights of the precipitates were expressed in % of the initial weight of monosaccharide.

For carrying out the huminification by dilute acids 5% solutions of the monosaccharides in acid of definite concentrations were prepared. 10 ml portions of these solutions were heated in small closed flasks on a boiling water bath. Experiments at higher temperatures were made in copper ampoules on a paraffin bath. The method otherwise was similar to that described earlier.

Preliminary experiments showed that even some minutes after dilution the reaction mixture formed rather coarse, rapidly-setting flocs of humin substance. About 95-98% separated in the first day and the rest in the course of the following 7-10 days. We restricted our attention to the main bulk of the humin substance.

Huminification of monosaccharides by concentrated sulfuric acid. The results of experiments at 20° and acid concentrations of 61.6, 72 and 78% are plotted graphically in Figure 1. It can be seen from them that individual monosaccharides form humin substances at different rates. The yields vary as well. The latter were determined as described above. The only difference was that the reaction was

terminated when the maximum quantity of humin substance had been obtained. In the concentration range 61.6-78% H_2SO_4 and a temperature of 20-60° they were practically constant for any given monosaccharide and equal to 62.5 for xylose, 52.6 for arabinose, 44.3 for galactose and 32.5% for glucose: thus the monosaccharides can be grouped in the following increasing order of yield of humin substance;

glucose < galactose < arabinose < xylose.

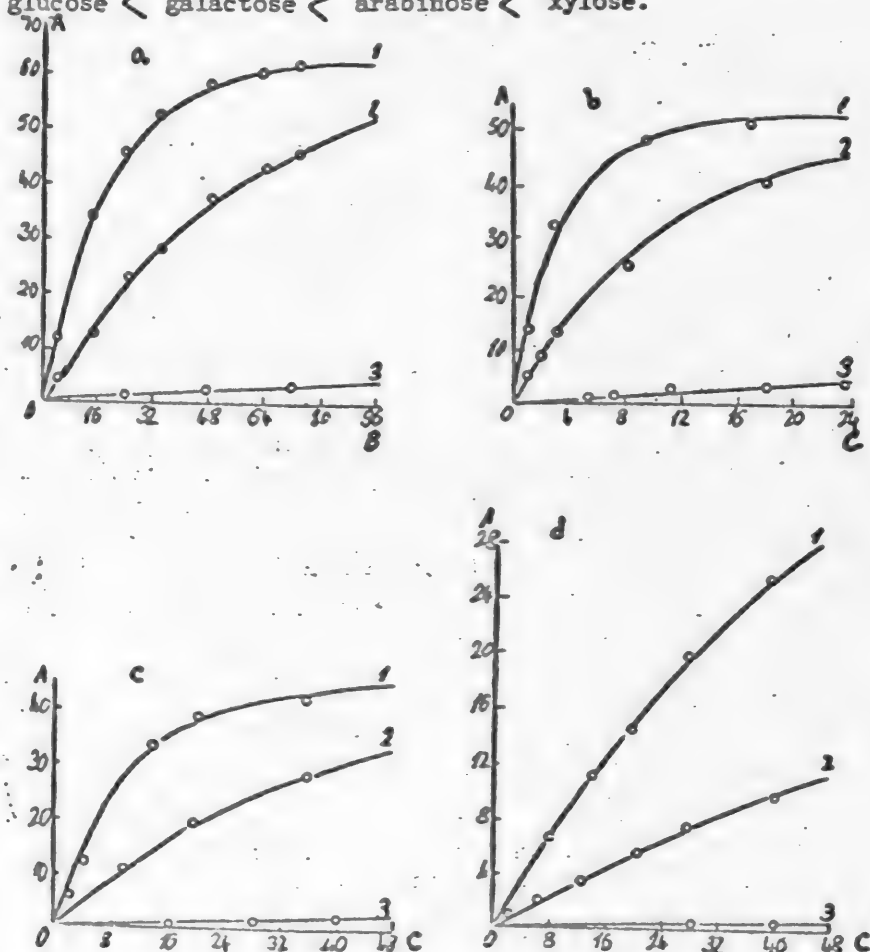


Fig.1. Humification of monosaccharides by conc. H_2SO_4 .

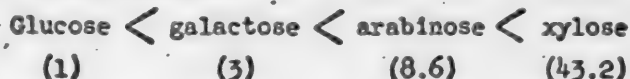
A) Content of humin substance (% of weight of sugar); B) time in hours; C) time in days. a) Xylose; b) arabinose; c) galactose; d) glucose. Acid concentration: 1) 78%, 2) 72%, 3) 61.6%.

If the data of Figure 1 are inserted in the formula for the rate of a first order reaction $x = a(1 - e^{-Kt})$, where a = limiting quantity of humin substance, x = quantity of humin substance formed during the given time interval (both expressed in % of the initial monosaccharides), then the calculated constants K for sulfuric acid of one and the same concentration for separate intervals of time agree rather well with one another (Table). However, since the yields of humin substance from monosaccharides differ greatly, comparison of the rate of huminification by comparison of the constants loses its meaning.

To assess the relative rates of development of humin substances we were

limited to a comparison of the quantity of them formed by 72% sulfuric acid in 24 hours from the start of experiment. This quantity was: for xylose 21.6, for arabinose 4.3, for galactose 1.5, and for glucose 0.5%.

The monosaccharide investigated can be arranged in the following order of increasing rate of huminification:



The figures in brackets indicate the ratios of the quantities of humin substances obtained.

Kinetics of huminification of xylose in sulfuric acid of different concentration at 20°

Duration of huminification (hours)	Humin substance obtained, % of weight of initial sugar	Humin substance obtained, in an interval of time x , (in %)	Quantity of initial sugar at the beginning of the time interval a , (in %)	Quantity of sugar at the end of the time interval, $(a-x)$ (in %)	Rate constant for huminification K based on time in hours
61.6% H_2SO_4					
72	2.9	4.6	100.0	95.4	0.00078
96	3.8	1.4	95.4	94.0	0.00062
120	4.7	1.4	94.0	92.6	0.00062
144	5.7	1.6	92.6	91.6	0.00069
168	6.6	1.4	91.0	89.6	0.00062
192	7.6	1.6	89.6	88.0	0.00072
216	8.5	1.4	88.0	86.6	0.00066
Mean.....					0.00067
72% H_2SO_4					
10	9.6	15.3	100.0	84.7	0.0167
20	18.0	13.4	84.7	71.3	0.0174
30	25.0	11.2	71.3	60.1	0.0170
40	30.8	9.3	60.1	50.8	0.0168
50	35.8	8.0	50.8	42.8	0.0173
60	40.0	6.7	42.8	36.1	0.0171
70	43.5	5.6	36.1	30.5	0.0168
Mean.....					0.0170
78% H_2SO_4					
5	13.8	22.0	100.0	78.0	0.0496
10	24.6	17.3	78.0	60.7	0.0501
20	39.5	23.8	60.7	36.9	0.0497
30	48.6	14.6	36.9	22.3	0.0503
40	54.0	8.6	22.3	13.7	0.0488
50	57.4	5.4	13.7	8.3	0.0494
60	59.4	3.2	8.3	5.1	0.0470
Mean.....					0.0493

Consequently the pentoses, especially xylose, were most quickly converted to humin. Galactose was converted three times faster than glucose. Comparison of the yields of humin substances and the rate of huminification show that the more rapidly they were formed from the monosaccharide the larger their yield.

The effect of concentrated sulfuric acid on the huminification of monosaccharide is shown in Figure 2a (for xylose). Within the limits of

60-80% monohydrate the rate constant for all monosaccharide increases by 1.4-1.5 times for every 2% rise in concentration of acid. Figure 2b shows the effect of temperature on the formation of humin substance (for xylose in 78% sulfuric acid). At 0° humin substance is not formed in any notable quantity. When the temperature is raised the reaction proceeds energetically. In the temperature interval of 20-40° the ratio of constants K_{40}/K_{20} fluctuates from 5 to 7.5; in the temperature interval 40-60° the ratio K_{60}/K_{40} is 9.4 for xylose, 14.7 for arabinose, 36.3 for galactose, and 41 for glucose.

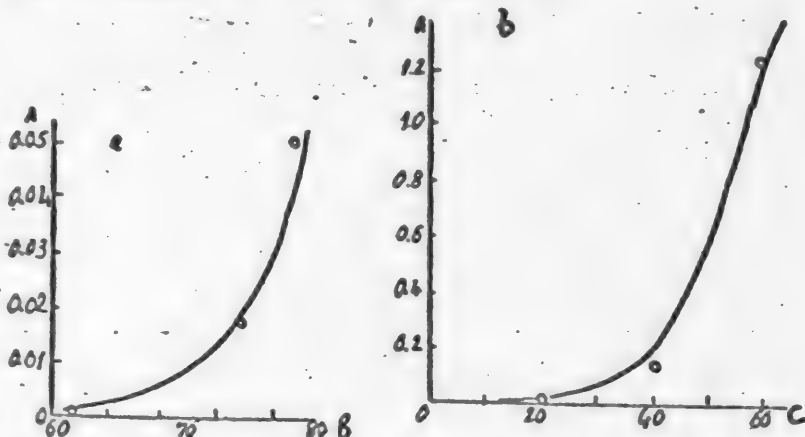


Fig. 2. Effect on the huminification of monosaccharides of: a) concentration of sulfuric acid; b) temperature.

A) Rate constant for huminification (K) (hour basis); B) H_2SO_4 (in %); C) temperature (°).

Huminification of monosaccharides by concentrated sulfuric acid. The yield of humin substances obtained with hydrochloric acid is somewhat less than with sulfuric acid and is, for example, 47.5% for xylose (instead of 62.5%). The formation of humin substance from xylose and glucose in 37.23% HCl at 20° is shown in Figure 3a. From the curve in Figures 1a, 1g and 3a, we find for xylose in 72% H_2SO_4 and 24 hours 21.6%, and in 37.23% HCl, 7.5% humin substances, i.e., a 2.4 times lower quantity in the latter case. In 61.6% sulfuric acid the huminification is considerably slower than in 37.23% HCl (amount of humin substances produced only 1.4%). If we take into account the dependence of the rate of huminification by sulfuric acid established above, then we can assume that 37.23% HCl should behave in the same way as 68.5-69% H_2SO_4 .

Sulfuric and hydrochloric acids would be more correctly compared at equivalent concentrations. At a content of 12.1 g - equiv/liter HCl the huminification of monosaccharide is 600-650 times as fast as by sulfuric acid of the same concentration.

Huminification of monosaccharides by dilute sulfuric and hydrochloric acids. It was found that the development of humin substances from monosaccharides in dilute acids at 100° is considerably slower than in concentrated acid at 20°. Thus after 24 hours 1 N sulfuric acid produced 4.1% from xylose whereas 72% acid produced 21.6%. However, 61.6% sulfuric acid huminifies monosaccharides 2.7 times as slowly as 1 N sulfuric acid. 66% H_2SO_4 causes the monosaccharide to form humin substances at about the same rate as 1 N H_2SO_4 at 100°.

As can be seen from Figures 3b, in 0.1 N HCl the rate of development of humin substance is approximately 3.2 times larger than in 0.1 N H_2SO_4 . Separate experiments show that when the concentration of HCl doubles the rate of

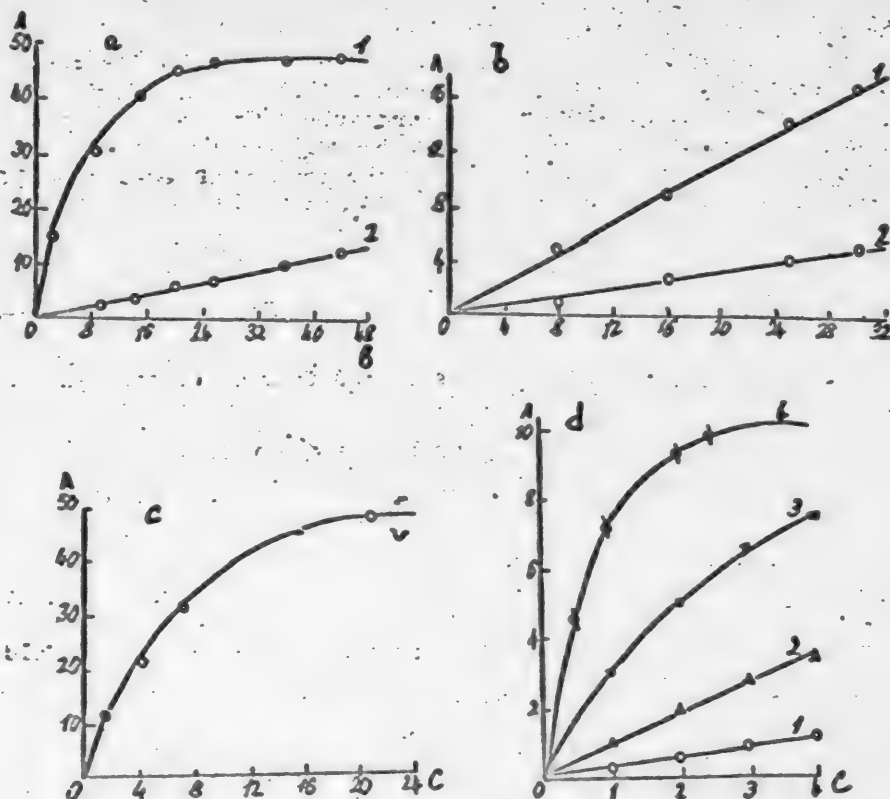


Fig.3. Rate of development of humin substances

A) Content of humin substances (in % by weight of sugar); B) time in days; C) time in hours. a) Action of 37.23% HCl at 20° on: 1 - xylose, 2 - glucose; b) action of 1 N solutions: 1 - HCl and 2 - H₂SO₄; c) action of 3.65 N or 12% HCl on xylose; d) action of 0.1 N HCl on glucose at temperatures of 1) 150°, 2) 160°, 3) 170°, and 4) 180°.

humification doubles, and with sulfuric acid the rate increases for example by a factor of 2.2.

Even in moderately concentrated acid (cf. Figure 3b for 3.65 N or 12% HCl and xylose) the humification is extremely fast. Thus at 100° after 8 hours in 3.65 N acid 35% humin is obtained but in 2 N acid only 10%. By increasing the concentration of acid 1.65 times the rate of reaction increases by a factor of 3.5.

In Figure 3d (for glucose in 0.1 N HCl) it is evident that for every 10° rise in temperature the rate of reaction increases 3.4 - 3.5 times; raising the temperature causes this reaction to become more energetic than increasing the acid concentration.

To assess the relative rates of formation of humin substances an experiment with 1 N HCl at 100° was carried out. The experiment lasted three hours. In this time 4.39% of humin substance was obtained from xylose, 1.13% from arabinose, 0.15% from galactose and 0.06% from glucose. Thus the monosaccharides investigated can be grouped according to their rate of humification in the same order as for the action of concentrated acids. Hahn's assertion [2] that the humification of galactose is somewhat slower than that of glucose is not

sufficiently proved.

The yield of humin substances in dilute acids at 100° is nearly the same as in concentrated acids. For example, for xylose in 2 N HCl it is 47.0%, and in 37.23% acid it is 47.5%. However, for temperatures above 100° the yield of humin substances decreases, and at 180° for glucose is only 10.3% on the weight of sugar. Consequently at high temperatures the process of breakdown of sugar takes predominance over the formation of organic acid.

SUMMARY

1) It has been established that the rate of huminification can be formally represented by an equation for a first order reaction.

2) It has been shown that humin substance is formed from monosaccharides at rates which increase in the order:

glucose < galactose < arabinose < xylose.

3) The rate of huminification depends on both the nature and concentration of the acids, and also on the temperature.

4) The yield of humin substances is not constant and is conditioned in concentrated acids mainly by the sugar and the character of the acid. In dilute acid at temperatures above 100° the breakdown of sugar predominates over the formation of organic acids and the yield of humin substances decreases 3-4 fold.

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